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SOME REGULARITIES OF THE CHANGE OF CATHODIC POLARIZATION DURING DEPOSITION OF METALS IN PRESENCE OF SURFACE-ACTIVE ADDITIVES

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The employment of colloidal and surface-active additives in electroplating has been practiced for nearly fifty years. As early as 1905, Senn[1] observed that the addition of glue or gelatin to solutions for electrolytic lead plating appreciably improves the uniformity and smoothness of the lead deposits at the cathode. Sieverts and Wippelmann [2] in 1912 carried out some experiments to clarify the reaction of colloids with metallic deposits at the cathode. Izgaryshev and co-workers [3-5] were the first to study the influence of surface-active agents on polarization during discharge of metallic ions and established a series of characteristic features of this phenomenon, thereby starting the systematic study of the effects of colloidal and surface-active agents on electrode processes and the structure of the electrolytic deposit.

At the present time certain colloids and surface-active agents are widely employed in electroplating practice and their action has been widely studied in many investigations. Among these we may mention in particular the work of Loshkarev and co-workers [6-9], Vagramyan [10], and Frumkin and his school [11-15]. In spite of the numerous researches in the field of the action of surface-active agents on cathodic polarization and the quality of the electrodeposits, there are still many unsolved theoretical and practical problems. To take but one example, due to the absence of rules, the selection and application of various organic and colloidal additives in solutions of electrolytes during electroplating of metals has been made on a purely empirical basis. Consequently further study of this problem, especially in association with the discovery of new methods of investigation, is fully justified and desirable.

Our present research is a first attempt to determine the velocity and magnitude of the change in cathodic polarization under the action of surface-active agents in dependence on their chemical composition and molecular structure. The additives selected for this study were the simplest aliphatic alcohols from methyl through amyl, and the mono- and dicarboxylic acids: formic, acetic, propionic, butyric, valeric, oxalic, malonic and succinic; their effect on the cathodic polarization of copper, silver, nickel and zinc was studied.

EXPERIMENTAL

Method of investigation. Experiments on electrolysis and changes of polarization were conducted in a rectangular cubic vessel with a capacity of 130 ml. To opposite sides of the vessel were attached (with pure paraffin wax) electrodes with a total active surface of 7 cm each. The anodes were plates prepared from analytically pure metals while the cathodes were sheet platinum densely coated with an electrodeposit of the metal under test. For the determination of changes of cathodic polarization, the auxiliary electrodes were of the same metals deposited electrolytically on platinum in the conditions used for preparation of the cathodes. Consequently, the electrolysis vessel, the intermediate vessel and the auxiliary electrode contained the same solution with ions of the investigated metal and, in the absence of a polarization current, the potential difference between the investigated cathode and the auxiliary electrode was practically zero. This eliminated the influence on the potential of trace amounts of any substances introduced with the reagents and permitted accurate determination of the change of potential of the cathode under the action of additives only introduced with the electrolyte subjected to examination.

The set of vessels with electrodes was placed in a thermostat in which the temperature was held at 25 ± 0.1°. The electrolyte in the electrolytic cell was stirred with a mechanical stirrer at a constant rate of 200 r.p.m. In the experiments with copper an electrolyte was used which consisted of 0.1 N $CuSO_4$ solution and 0.1 N H_2SO_4. Experiments with zinc were conducted in 1N $ZnSO_4$ solution; with nickel in 1N $NiCl_2$ with silver in 0.5 N $AgNO_3$ solution. All the substances were used in the analytically pure grades and were further purified by recrystallization (by distillation if liquid).

Measurements of the velocity and magnitude of changes of polarization potential. Measurements of the rapid changes of the potential of deposition of ions of the investigated metal on introduction of the additives into the electrolyte were performed by the compensation-oscillographic method. The principle of the apparatus developed and of the connecting-up of the 3-loop mechanical oscillograph in the general measuring scheme are represented in Figure 1.

In the latter, P is the electrolysis cell; C is the auxiliary electrode, Y is the three-lamp amplifier; T_1T_5 are the loops of the mechanical oscillograph; Ak_1, Ak_2, Ak_3 are accumulators; E_0 is an electromagnetic break with the frequency of oscillation of alternating mains current, i.e. 50 periods sec.

Since the change of cathodic polarization could be increased by the amplifier Y by several powers of ten up to $(25)^3$ times, before each experiment after establishment of a constant heating and a specific anodic voltage of the cathode tubes in the amplifier, calibration was carried out of the oscillograph recordings. Use was made for this purpose of a potentiometer B consisting of a resistance box R_4 inserted in the circuit of the amplifier and the oscillograph by means of the switch n. By giving definite potentials at the terminals of the amplifier Y, the amplitude was noted of the light traces on the drum of the oscillograph and the corresponding curve was plotted and then served for evaluation of the changes of cathodic potential in the electrolysis cell P. After the oscillographic traces had been calibrated the switch n was shifted to contact a so that the amplifier Y and the oscillograph were connected into the measuring circuit and the variable resistance R_6 was used to establish a determined current density at cathode K. Then, after compensation of the difference of potentials between cathode K (being polarized) and the auxiliary electrode, the potentiometer A was used to introduce into the electrolysis cell P an exactly predetermined amount of surface-active additive and the change of cathodic potential was recorded on the oscillograph drum. Consequently our method of measurement permitted precise determination of the rise or fall of cathodic polarization, depending exclusively on the action of the introduced additives at any desired current density, and also enabled the change of this potential to be followed in the course of any desired interval of time.

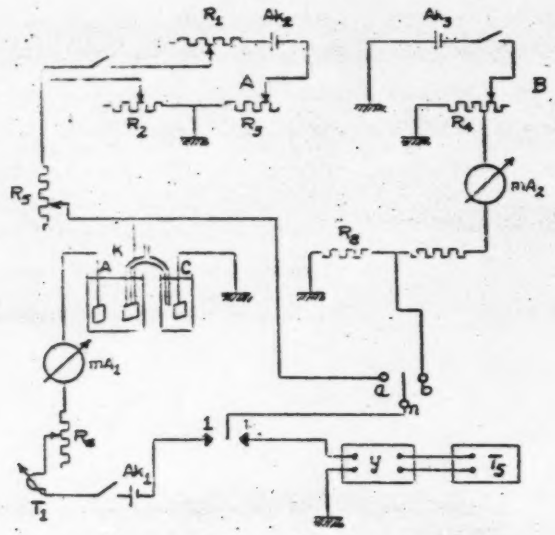

Fig. 1. Set-up of compensated oscillographic apparatus for measurement of magnitude and velocity of change of polarization.

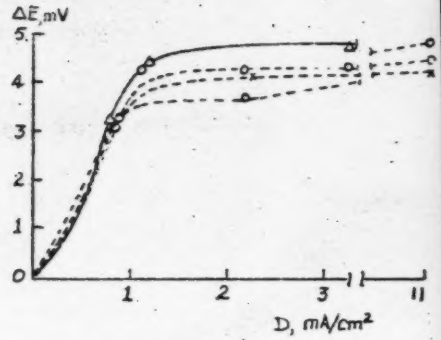

Fig. 2. Dependence of shift of cathodic potential of copper, on addition to the electrolyte of organic acids, on the current density: o – 25,16 mM/l CH_3COOH; x – 6,26 mM/l CH_3CH_2COOH; • – 5,8 mM/l $CH_3CH_2CH_2COOH$; Δ – 2,6 mM/l $CH_3CH_2CH_2CH_2COOH$

EXPERIMENTAL RESULTS AND THEIR EVALUATION

The change of cathodic potential under the action of surface-active admixtures depends up to a certain degree on their amount, on their chemical composition and on the current density. This dependence is illustrated in Figures 2 to 4. In Figure 2 are plotted data which show the increase of cathodic polarization when copper is precipitated as the result of introduction into the electrolyte of definite amounts of acetic, propionic, butyric and valeric acids at various current densities, the amounts of introduced acids being so selected that the deposition potential of the copper ions increased approximately by the same amount. As we see from Figure 2, with unchanged concentration of additive the shift of cathodic potential remains substantially constant and does not change with further rise of current density. The form of the curves is identical for all the additives studied. It may be noted that, in the present case, valeric acid is roughly 9,5 times as active as acetic acid. Propionic and butyric acids take up an intermediate position in respect of activity.

With increase of concentration of the same acids as additives with unchanged current density, the change of the cathodic potential of copper follows a curve similar to an adsorption isotherm. These curves, which were plotted for acetic and propionic acids at a current density of 0.71 mA cm^2 are shown in Figure 3. Side by side with them are given the curves 3 and 4 which were plotted for the same acids at a current density of 7.1 mA cm^2. A comparison of curves 1 and 3 and of 2 and 4 clearly shows that the very same amount of acetic or propionic acid, introduced as additive, brings about a shift of cathodic potential of copper which is the greater the higher the current density at the cathode. Consequently, with increasing current density, the adsorption of those acids at the surface of the cathode increases. This phenomenon was also observed in the case of butyric, valeric, oxalic, malonic and succinic acids on copper cathodes; in all probability it depends on the increase in the actual surface of the cathode and on the growth thereon of a number of active centres when stronger currents are passed through.

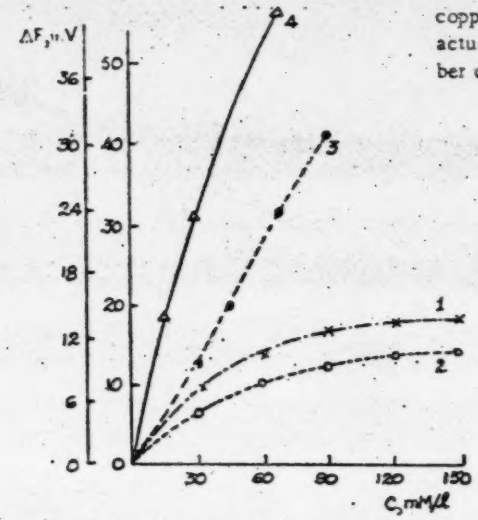

Fig. 3. Magnitude of change of potential of copper deposition as a function of the amount of acetic and propionic acids introduced as additives into an acidified solution of copper sulfate: 1 - with addition of acetic acid; 2 - with addition of propionic acid at a current density of 0.71 mA /cm^2; curves 3 and 4 are similar curves obtained at a current density of 7.1 mA/ cm^2.

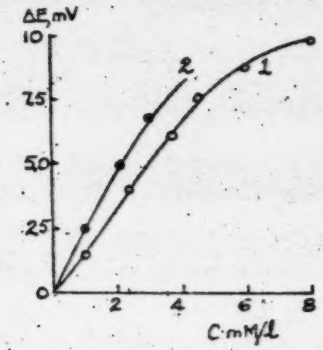

Fig. 4. Magnitude of change of deposition potential of copper as a function of the amount of malonic and butyric acids introduced into the electrolyte as additives, at a current density of 3.7 mA /cm^2 1 - with addition of malonic acid; 2 - with addition of succinic acid.

As already remarked, on introduction of fatty acids as additives, the jump in cathodic potential ΔE at constant current density increases with the rise in the number of carbon atoms in the homologous series. This is directly apparent when we examine the curves in Figs. 2-4. The plots in Fig. 4 show the change in cathodic potential as a function of the concentration of the added dicarboxylic acids – malonic (1) and succinic (2) – at a constant current density of 3.7 mA /cm^2. We see from Fig. 4 that the activity of the additives is not only a function of the number of carbon atoms in the homologous series but is also markedly dependent on the number of polar groups in the molecule. This is also very clearly brought out by the data in the table which show the amounts of acetic, propionic, malonic and succinic acids in mM/l needed for raising the cathodic potential of copper ΔE by 2,4, and 5.5 mV with an unchanged current density of 3.7 mA/ cm^2.

TABLE

Amounts of Acids Needed to Change the Potential of Copper by 2, 4, and 5.5 mV.

Δ in mV	Concentration of acids in mM / liter			
	acetic	propionic	malonic	succinic
−2	15	2.6	1.2	0.8
−4	35	8.0	2.4	1.5
−5.5	50	13 .0	3.3	2.25

An examination of the numerical data in the table, as well as in Figs. 3 and 4, immediately shows that for the attainment of a uniform effect, i.e. a rise in cathodic polarization by the same amount along the rising portion of curve E — C, the organic acids are arranged in a strictly defined order; the longer the chain of a homolog, the lower is its concentration, which promotes an identical cathodic overvoltage. Furthermore, the dicarboxylic acids are roughly 3.5 to 15 times as active as the monocarboxylic acids with the same number of carbon atoms in the molecule. Consequently, the presence of an additional carboxylic acid group in the acid molecule considerably increases its surface activity in the conditions here considered. Comparing the concentration for one member of the homologous series c_n with the concentration of the next member c_{n+1}, causing an identical shift of cathodic potential at an identical current density, we obtain the ratio c_n / c_{n+1} which lies within the limits of 1.9 to 5.8 for monocarboxylic acids and 1.50 to 1.75 for dicarboxylic acids. Hence at low concentrations of the organic acids used as additives, with the exception of the first members of the two series (oxalic and formic acids), and at low current densities, we find approximate applicability of Traube's law to the change of the cathodic deposition potential of copper ions from acid solutions. This is one more confirmation of the interdependence between the potential difference between metal and solution (on the one hand) and the adsorption phenomena in the boundary layer (on the other hand), the theory of which has been successfully developed by Frumkin.

It must be pointed out that dicarboxylic acids differ from monocarboxylic acids not only in their degree of activity but also in the character of their action upon the rate of change of cathodic potential. This is very clearly illustrated by plotting oscillograms which show the change of potential with passage of time after introduction of the additives. A few of these oscillograms are shown in Figures 5 and 6. The curves in Figure 5 represent the rate of change of the cathodic potential of copper ΔE after introduction into the electrolyte of 3.76 and 7.52 mM/l of malonic acid at a current density of 3.7 mA/cm^2, while Figure 6 contains similar curves in illustration of the potential change after addition of 0.81, 1.64 and 3.29 mM/l succinic acid at the same current density at the cathode; as in the previous diagrams, the zero value on the axis of the abscissas corresponds to the cathodic potential at the given current density in the absence of additions of organic acids to the electrolyte. The change of cathodic potential everywhere takes place in the direction of increase of its negative value.

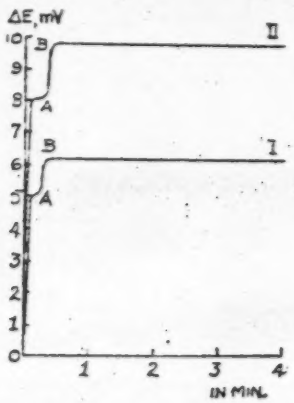

Fig. 5. Rate of change of deposition potential of copper after introduction into the electrolyte of malonic acid at a cathodic current density of 3.7 mA/cm^2: I - 3.76 mM/l; II - 7.52 mM/l.

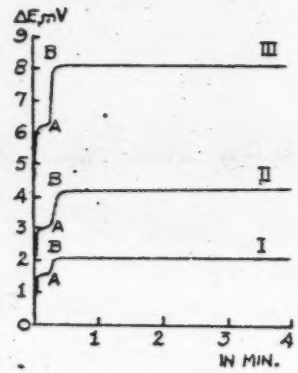

Fig. 6. Rate of change of deposition potential of copper after introduction into the electrolyte of succinic acid at a current density of 3.7 mA/cm^2: I - 0.81 mM/l; II - 1.64 mM/l; III - 3.29 mM/l.

As we see from these diagrams, within only a minute after introduction into the electrolyte of the dicarboxylic acids, with stirring of the electrolyte at a speed of 200 r.p.m., two jumps of cathodic potential occur in rapid succession. The height of these jumps depends on the amount of acid added. The higher the concentration of malonic or succinic acid in the electrolyte at the given current density, the higher the initial potential jump A and the greater the distance AB between the two jumps. It should be noted that with monocarboxylic acids, two analogous jumps are not observed. After the first jump the ΔE versus time plot abruptly bends over and runs the whole time parallel to the abscissas.

This new and interesting phenomenon, observed with dicarboxylic acids, clearly points to a definite interrelation between the change of cathodic polarization and the specific structure of the additives employed. At present it cannot be otherwise explained than by a type of adsorption peculiar to molecules containing two polar groups. It may be suggested that at the start the molecules of dicarboxylic acid adsorbed on the surface of the cathode are orientated with only one carboxyl group parallel to the surface. After a certain, fairly short, period of time, the molecules undergo rearrangement in the adsorbed film and the other carboxyl group becomes more firmly bonded to the surface of the metal. Due to this the same number of adsorbed molecules more completely fill the surface of the metal and brings about the second sharp potential jump at the cathode.

Additions of lower organic acids act on silver cathodes in exactly the same way as on copper cathodes, i.e. they increase the polarization potential. Experiments with silver cathodes were carried out using platinum electrodes coated with an electrolytically dense layer of silver deposited from cyanide solutions. Polarization measurements were performed in 0.5 N silver nitrate solution. In Figure 7 are shown the oscillograms for the rate of change of polarization when the electrolyte contains definite amounts of acetic (I), propionic (II) and butyric (III) acids and a constant current density of 3 mA/cm^2 is maintained. The quantities of acids added were so selected that approximately equal changes of cathodic potential were caused. The curves show that introduction of the additives brings about a sudden rise of polarization quickly followed by a fall to the original value. This penomenon, not observed in work with other metals, corresponds entirely to Vagramyan's observation of passivation of crystals of silver during its electrodeposition [16]. Once again it confirms his explanation of the causes of passivation.

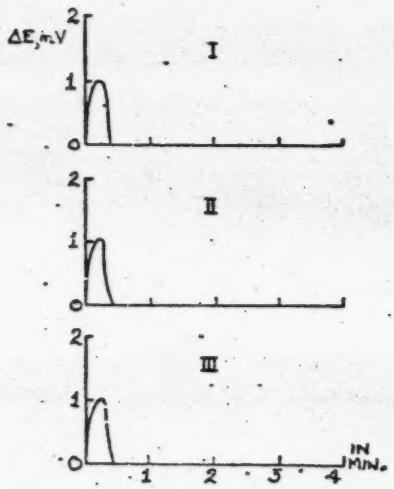

Fig. 7 Magnitude and velocity of change of precipitation potential of silver on addition of organic acids to the electrolyte: I - 12.72 mM/l acetic acid; II - 4.02 mM/l propionic acid; III - 1.5 mM/l butyric acid. Current density of 3.0 mA/cm^2

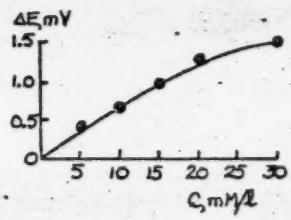

Fig. 8 Rise of original jump of the precipitation potential of silver with increase of concentration of the propionic acid added to the electrolyte at a cathodic current density of 1.43 mA/cm^2

From the curves of Fig. 7 it can readily be seen that the ratios of concentrations of acids causing the original jump of polarization potential by the same amount at constant current density is in accord, as in the case of copper, with Traube's law. Furthermore, the rise of the original potential change with increasing amounts of added acid at constant current density is represented by a curve similar to an adsorption isotherm. An example of this type of curve, plotted for propionic acid at a current density of 1.43 mA/cm^2, is presented in Figure 8.

The experiments described show that the nature of the action of the very same additives on the polarization of copper and silver cathodes is dissimilar. This difference is even more conspicuously manifested in the case of the cathodic polarization of zinc and nickel. Additions of lower organic acids to 1 N solution of zinc sulfate and 1N solution of nickel chloride do not raise the cathodic polarizations of zinc and nickel but considerably lower them. The polarization during cathodic precipitation of zinc is lowered to a relatively greater extent by the higher members of the homologous series of acids. For example, at low cathodic current densities, the addition of butyric acid lowers the polarization during precipitaion of zinc about twice as much as on addition of the same amount of acetic acid. It should be noted that the introduction of lower organic acids into zinc sulfate solution appreciably lowers the pH of the electrolyte and much hydrogen begins to be evolved at the cathode at the same time as the zinc is

deposited. The concomitant evolution of hydrogen and the relatively small effects of the potential change preclude the possibility of precise determination of any quantitiative regularities similar to those established for copper and silver cathodes.

The hydrogen evolution accompanying the main process still more conceals the general picture of the phenomena when working with nickel cathodes. On nickel cathodes it was impossible to establish any specific action of the added acids. Each acid lowers the cathodic polarizaton of nickel approximately in proportion to the fall in pH of the solution. For example, additions of hydrochloric acid and propionic acid to 1N nickel chloride solution reduce the polarization of nickel by approximately the same amount if the pH of the electrolytes are brought to identical values.

In order to avoid the complications resulting from evolution of hydrogen at zinc and nickel cathodes when using lower acids as additives, experiments were carried out with additions of lower alcohols of the aliphatic series. It was found that methyl, ethyl, propyl, butyl and amyl alcohols do not manifest any action on the polarization during precipitation of silver and nickel at any current densities. Their effect on the polarization of copper cathodes is in the same direction as that of the organic acids, i.e. they render the deposition potential of copper more negative. Although the potential shift of copper on addition of alcohols to the solution is less than on addition of acids, the same regularities of change of polarization could be observed except in the case of methyl alcohol, as were found with acids, namely, the applicability of Traube's law and the possibility of representation of the potential change as a function of the concentration of additives at low current densities by curves similar to adsorption isotherms. The curves for copper cathodes obtained with alcohols do not differ essentially from the corresponding curves with acids and are therefore not reproduced here.

The results obtained with zinc are very similar in character. In Figure 9 are plotted curves representing the magnitude and velocity of change of the cathodic potential of zinc after introduction into a 1N zinc sulfate solution of 65 mM/l of the alcohols mentioned at constant current density. Here, as in the preceding diagrams, the zero line denotes the polarization potential of zinc in pure $ZnSO_4$ solution without additives, at a current density of 5.7 mA/cm^2. As we see from the diagram, additions of propyl, butyl and amyl alcohols appreciably raise the polarization during zinc deposition. The higher members of the homologous series of alcohols are roughly 2-2.5 times as active as the lower members at the same current density. An exception arises with the first two members of the series (methyl and ethyl alcohols). Methyl alcohol lowers the polarization by about 0.5 mV while the second manifests no action at all. The cause of the different course of the curve of amyl alcohol is evidently its low solubility in water and aqueous solutions.

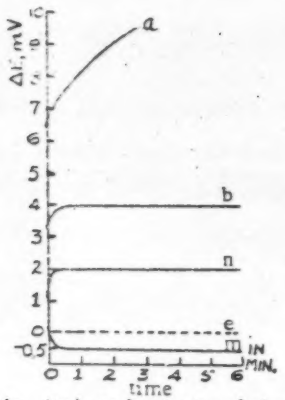

Fig. 9 Magnitude and velocity of change of deposition potential of zinc after introduction into the electrolyte of alcohols: m - 1N ZnSO + 65 mM/ l CH_3OH; e – 1N $ZnSO_4$ + 65 mM/1 CH_3CH_2OH; n - 1 N $ZnSO_4$ + + 65 mM/1 $CH_3CH_2CH_2OH$; b - 1 N $ZnSO_4$ + 65 mM/1 $CH_3CH_2CH_2CH_2OH$; a - 1 N $ZnSO_4$ + 65 mM/1 $CH_3CH_2CH_2CH_2CH_2OH$. Current density 5.7 mA/cm^2.

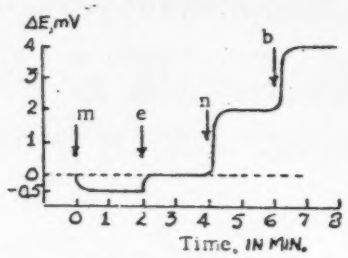

Fig. 10 Change of deposition potential of zinc on successive addition of alcohols to the same electrolyte: m – 65 mM /1 CH_3OH; e – 65 mM/1 CH_3OH + 65 mM /1 CH_3CH_2OH; n – 65 mM/1 CH_3OH + 65 mM/1 CH_3CH_2OH +65 mM/1 $CH_3CH_2CH_2OH$; b – 65 mM/1 CH_3OH + 65 mM /1 CH_3CH_2OH + 65 mM/1 $CH_3CH_2CH_2OH$ + 65 mM/1 $CH_3CH_2CH_2CH_2OH$.

It is interesting to note that successive introduction of one alcohol after another into the same portion of zinc sulfate solution leads to stepwise change of potential. Addition of a definite amount of a higher homolog of the alcohol series causes a potential change whose magnitude does not depend on the presence in the solution of a lower alcohol. This is illustrated by the plot in Figure 10: at point m 65 mM/liter methyl alcohol was added to the solution; after a period of 2 minutes addition was made to the solution of 65 mM/liter ethyl alcohol, followed after 4 minutes by 65 mM/liter propyl alcohol, and after a further 6 minutes by 65 mM/liter butyl alcohol. The current density throughout the whole of the experiment was kept constant at 5.7 mA/cm^2. This interesting phenomenon clearly indicates the displacement of an alcohol by the next highest homolog from the surface of the electrode, since the higher alcohols have a greater surface activity and are more firmly adsorbed at the surface of the metal.

SUMMARY

1. A compensation-oscillographic method has been developed for measuring the magnitude and velocity of polarization changes on introduction of various additives into an electrolyte during electrolysis. This method was used to investigate the influence of simple organic compounds (formic, acetic, propionic, butyric, oxalic, malonic and succinic acids and methyl, ethyl, n-propyl and n-butyl alcohols), introduced as additives, on the cathodic polarization during deposition of copper, silver, zinc and nickel within the current density range of 1 to 10 mA/cm^2.

2. It was established that the rise of cathodic polarization on precipitation of copper with rising concentration of the acids and alcohols added to the electrolyte at constant current density not exceeding 10 mA/cm^2 follows a curve similar to an adsorption isotherm. The absolute magnitudes of the shift of cathodic potential provoked by introduction into the electrolyte of definite amounts of acids and alcohols of the same homologous series obey Traube's law. The very same regularities were established for silver cathodes under the action of lower organic acids, and for zinc cathodes under the influence of lower primary alcohols with the exception of methyl and ethyl alcohols.

Admixtures of organic acids cause only a temporary change of potential during deposition of silver following their introduction. This jump quickly falls to zero in the first half minute after addition of the acid to the electrolyte, i.e. the potential reverts to its original value.

3. It was observed that addition of the first members of the dicarboxylic acid series to the acidified copper sulfate solution causes a double jump in the cathodic polarization of copper which proceeds during the first 10–15 seconds after addition of the acid. It is suggested that this new phenomenon is associated with a specific course of adsorption of the dicarboxylic acids at the metal surface, involving bonding of the two carboxyl groups to the surface with differing degrees of firmness.

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THERMOCHEMISTRY AND STRUCTURE OF ATOMS

COMMUNICATION 7. INVESTIGATION OF THE CARBONATES OF THE SECOND (MAIN) GROUP OF THE MENDELEEV SYSTEM

A. F. Kapustinsky and M. S. Stakhanova

INTRODUCTION

Consideration was given in one of the preceding communications to the application of the rule of thermochemical logarithmicity [1] to oxalates of alkaline earth metals [2]. In the present paper we develop the investigation with reference to the carbonates of the same elements in view of the particular practical and theoretical importance of these compounds in metallurgy, in the chemistry of building materials and in geochemistry. This paper includes in part the results not only of calorimetric measurements but also of our earlier determinations (made with the help of other methods) of thermodynamic constants of the carbonates of beryllium [3] and strontium [4,5]. The critically carried out systematization of the experimental data enabled the thermodynamics of the above-mentioned carbonates to be summarized; it also permitted the constants obtained to be generalized in the light of the rule of thermochemical logarithmicity and allowed a number of conclusions about the properties of the carbonate ion to be drawn.

The thermodynamics of the alkaline earth carbonates has been dealt with by many investigators, but in the majority of cases the measurements are not sufficiently accurate so that not only do serious discrepancies arise in the same type of measurements but there are unexplained deviations between calorimetric and high-temperature determinations of thermodynamic constants. This is illustrated by the monograph (documented in detail) of Kelley and Anderson [6]. Since the publication of the latter work, no substantial changes have taken place in this field, which circumstance made it not only desirable but even necessary that the present investigation should be undertaken.

EXPERIMENTAL

1. METHOD OF INVESTIGATION

Heats of formation were determined by studying the thermal effects of dissolution of finely crystalline (synthetic) $MgCO_3$ and $BaCO_3$ in 1 M solution of HCl at 25°. The hydrochloric acid was previously saturated with carbon dioxide at atmospheric pressure. The correction for evaporation of water was made as in the paper of Kapustinsky and Desideryeva [4]. In the case of $MgCO_3$ special attention was given to determination of the heat of solution of MgO in HCl.

The following changes were made in the calorimeter previously described by Kapustinsky and Klokman [7]. The thermostat was a Bose casing supplied with water from an adjacent thermostat with the aid of a water turbine. The temperature of the thermostat was maintained at 25 ± 0.005°. Current (120 V) was applied (Fig.1) to the heating spiral of the thermostat H; a vacuum relay VR was connected in series. The winding of the latter was connected to the tube (6F6) of an electrical relay whose heating circuit was supplied by the step-down transformer T, while the anode circuit was fed from the 120 V mains. Under normal emission the vacuum relay was switched in. On closing the contact of the thermoregulator TR (25°), however, the tube circuit was short-circuited, the amplification of the emission led to amplification of the current in the series winding of the vacuum relay, which breaks the contact in the main circuit and cuts out the heating spiral. The fall of temperature leads to closing of the circuit operating through the thermoregulator and consequently to resumption of heating. Since the current strength in the anode-mains circuit does not exceed $5 \cdot 10^{-4}$ A, there is no risk of burning-out of the contacts and of damage to the thermoregulator.

The calorimeter was a pyrex glass beaker, volume 0.45 l, closed with an ebonite stopper through which passed a Beckmann thermometer, a glass propeller stirrer, the leads of a Vrevsky mercury spiral, a glass tube with a bulb at the end containing a weighed amount of the substance, and a thin test tube for introduction (if needed) of freezing

mixture. The energy introduced for determination of the heat capacity of the solution was measured with the help of a potentiometric circuit which enabled alternate measurement of the voltage at the terminals of the divider and of standard resistance at definite intervals throughout the main period. The electrical measuring circuit (Fig. 2) consisted of a Rapp potentiometer II, a standard Weston element N, a 1-ohm standard resistance $R_{stand.}$, a resistance box r_1, r_2, and a mirror galvanometer G with a sensitivity of 10^{-9} A. In the diagram are also shown the calorimeter heater $R_{spir.}$, the loading resistances $R_{load.}$, the rheostats R_1, R_2, the ammeter A, the switch and circuit switches k, k_1, k_2 and a battery of lead accumulators (6V). Current strength and voltage were measured to an accuracy of 0.0001 A and 0.0001 V for total effects of the order of 0.8 A and 0.5 V.

The temperature was measured with a Beckmann thermometer (calibrated against a standard instrument in VIMS) with the aid of a cathetometer to an accuracy of $\pm$ 0.001° for a rise of the order of 0.4°; the time was measured to an accuracy of 0.1 seconds for periods of 3 to 4 minutes. All the electrical measuring instruments were checked before the start of the work in the Weights and Measures Department and were provided with certificates. The stop watch was regulated against an accurate time signal; it was connected to the circuit by the usual switch scheme [8]. The operation of the apparatus and the introduction of corrections for radiation, also the mode of computation, are as described in the literature [7, 8, 9].

The apparatus was calibrated by an electrical method and against the heat of solution of potassium chloride. At the conclusion of an experiment, the temperature of the calorimeter was brought to the initial temperature and the water equivalent of the system was determined in conditions similar to those prevailing for determination of heats of solution. The accuracy of the determinations (heats of solution), allowing for the characteristics of the instrument that we used, the amounts of heat evolved and the weights of reagents, ranged from 0.6 to 1.6% (with MgO and $MgCO_3$) and to 3% (with $BaCO_3$).

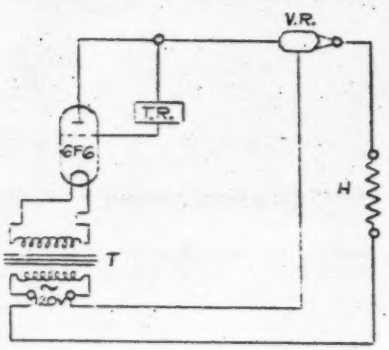

Fig. 1.

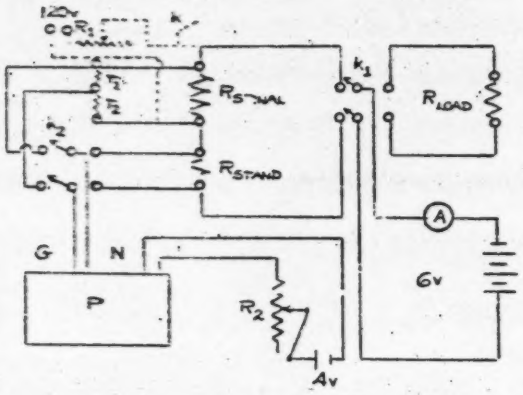

Fig. 2

A special place is occupied by the thermal investigation of beryllium carbonate which we described elsewhere [3] and the results of which are set forth in this paper. As is usual in investigations of dissociation equilibria, accurate allowance for all factors is impossible and moreover calorimetric measurements are impracticable in this case. Nevertheless we consider it to be necessary to again draw attention to the arguments in support of the trustworthiness of our previous investigation: a) satisfactory maintenance of the linear dependence of log K on 1/T; b) reproducibility of the results on approach to equilibrium both from the low- and the high-temperature side; c) non-dependence of the results on the degree of reduction of the weighed specimens (indicating absence of solid solutions); d) the crystallinity of the substances, confirmed both by microscopic and by X-ray examination (Fig. 3). The same may be said about the investigation of $SrCO_3$. An approximate evaluation in both cases gives an accuracy of determination of the heats of dissociation of 5 - 7%.

2. STARTING SUBSTANCES

a) Beryllium carbonate. We have already published a short account of the investigation of beryllium carbonate [3]. Here we limit ourselves to giving the X-ray diagram (Fig.3) which testifies to the crystallinity of the material used.

Fig. 3.

Fig. 4.

b) Magnesium carbonate. An attempt to utilize natural magnesite from the Satinsky deposit as starting material was unsuccessful because it is deficient in reactivity and even the purest specimens contain some pyrite.

Crystalline magnesium carbonate, free from basic salts, was prepared by two methods which gave identical results.

1) Solutions of chemically pure magnesium sulfate and chemically pure sodium carbonate were mixed at 80-100°. The resultant amorphous precipitate was washed several times on the filter with hot water, drained and dried. The dry precipitate was mixed with an equal volume of urea and heated for 2 hours at 140 - 145° in a porcelain crucible. Heating with urea converts the amorphous precipitate of basic salt into the crystalline form. The residues of hygroscopic water entered into reaction with the urea. On cooling, the caked mass was pulverized and repeatedly decanted to remove the urea and the turbidity due to non-crystallizing carbonate. After washing, the precipitate was dried at 100°.

2) The basic carbonate, again prepared from a boiling solution of magnesium sulfate and soda, was dried and then heated in a current of dry and pure carbon dioxide at 150° for 5 hours. After cooling in a carbon dioxide atmosphere, the carbonate was washed by decantation and then dried in the same apparatus in a CO_2 stream until constant in weight. The crystalline character of the prepared material was clearly confirmed both by microscopic and X-ray examination (Fig.4). Analysis gave a purity of 99.7%.

c) Magnesium oxide. The magnesium oxide (Kahlbaum) at our disposal was analyzed for its content of carbonate and moisture. Heating of two parallel samples at 1100° revealed the presence of 12.3% volatiles (carbonate decomposed by heating and moisture). Therefore for the thermochemical experiments we used the calcined oxide which, however, had not lost its reactivity. Magnesium was determined in the calcined sample by the pyrophosphate method. The results obtained (60.4% magnesium instead of theoretical value 60.3%) demonstrated the high purity of the starting material.

d) Strontium carbonate. Preparation and analysis have been described elsewhere [14].

e) Barium carbonate. Anhydrous, crystalline barium carbonate was obtained by reacting solutions of barium chloride and potassium carbonate (chem. pure recrystallized substances) at 80 - 100°. The precipitate was kept at the same temperature for several hours for growth of the crystals and washed on a porous-glass filter. The wash liquors were tested for their content of chlorine ion. The washed precipitate was dried at 150 - 160°. Barium was determined as sulfate. The preparation had a purity of 99.6%.

f) Water and hydrochloric acid. The water was a double-distilled grade which we also used in the syntheses and in calorimetry. The hydrochloric acid (1M) was saturated with a slow stream of well-purified carbon dioxide which was passed through for 14-16 hours. Prior to each experiment the requisite amount of this acid was subjected to supplementary saturation with CO_2 (2-2½ hours) at 25°. The completeness of saturation was checked by titrating a small sample of the acid with caustic alkali solution.

3. Results of Calorimetric Determinations

In Table 1 are summarized the results of experiments with magnesium and barium carbonates.

The results obtained correspond to the reactions:

$$MgCO_{3(solid)} + 2HCl_{(1:55)} = MgCl_{2(1:2000)} + H_2O_{(liq.)} + CO_{2(gas)} + 12800 \pm 200 \text{ cal.} \quad (1)$$

$$BaCO_{3(solid)} + 2HCl_{(1:55)} = BaCl_{2(1:2200)} + H_2O_{(liq.)} + CO_{2(gas)} + 3370 \pm 110 \text{ cal.} \quad (2)$$

In order to calculate the heats of formation of the carbonates, we sum the heats of formation of the constituents of each system [13] with the effects that we observe:

$$\Delta H^\circ MgCO_{3(solid)} = \Delta H^\circ MgCl_{2(1:2000)} + \Delta H^\circ H_2O_{(liq.)} + \Delta H^\circ CO_{2(gas)} - 2\Delta H^\circ HCl_{(1:55)} - \Delta H,$$

$$\Delta H^\circ MgCO_{3(solid)} = -260.4 \text{ kcal/mole.} \quad (3)$$

$$\Delta H^\circ BaCO_{3(solid)} = \Delta H^\circ BaCl_{2(1:2200)} + \Delta H^\circ H_2O_{(liq.)} + \Delta H^\circ CO_{2(gas)} - 2\Delta H^\circ HCl_{(1:55)} - \Delta H,$$

$$\Delta H^\circ BaCO_{3(solid)} = -287.3 \text{ kcal/mole.} \quad (4)$$

From an inspection of the errors of determinations of the heats of formation of the reaction components, we may assume the limit of experimental accuracy of determinations of heats of formation of carbonates to be 0.3-0.4%, equivalent to a fluctuation of about one large calorie in the indicated magnitudes.

TABLE 1

Heats of Solution of Carbonates in 1 M HCl at 25° (with Correction for Evaporation of Water) in cal/mole.

Wt. in g	Wt. of H_2O, in g	Δt_1 (dissolution of carbonate)	Correction for radiation, in %	Δt_2 (determination of thermal equivalent of system)	Correction for radiation, in %	Thermal equivalent of system, in cal/degrees	Heat of solution, in cal/mole
			Magnesium Carbonate				
$MgCO_3$							
0,9640	400,10	0,344	1,35	0,351	1,3	422,5	12840
1,0290	400,00	0,370	2,1	0,386	6,9	415,8	12760
1,0240	400,09	0,370	6,0	0,350	4,1	418,6	12820
1,0265	400,38	0,356	3,4	0,318	0,8	427,8	12610
0,9445	400,25	0,341	3,3	0,240	5,0	425,4	13000
0,9498	400,00	0,340	1,6	0,338	0,5	418,3	12730
			Mean 12800 ± 200 cal (± 1,6%)				
			Barium Carbonate				
$BaCO_3$							
3,5041	400,51	0,144	3,3	0,358	3,4	413,6	3440
3,4822	400,85	0,136	0,51	0,463	1,46	415,7	3290
3,6378	400,62	0,151	0,86	0,197	0,3	414,3	3480
3,5013	400,72	0,144	0,4	0,194	0	414,0	3440
3,1980	399,25	0,128	1,9	0,101	5,3	402,4	3270
3,3650	401,35	0,133	0,7	0,218	0	419,7	3350
3,2591	400,99	0,128	1,6	0,279	0	417,7	3320
			Mean 3370 ± 110 cal (± 3%)				

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One of the aims of the present investigation was the establishment of the heat of dissociation of carbonates into MeO and CO_2; this requires, apart from the data set forth above, a knowledge of either the heat of formation of the metallic oxide or the heat of its dissolution in HCl. Since among the materials that we investigated an especially important one for industry is $MgCO_3$, we undertook a determination of the heat of solution of MgO in hydrochloric acid in conditions close to those prevailing in the experiments on dissolution of $MgCO_3$. This leads to more accurate results because the summation of the heats of the two latter processes directly gives the heat of dissociation.

The weight of the sample of oxide was so selected that the concentration of magnesium chloride in solution corresponded to its concentration on dissolution of the carbonate (1:2000). The procedure for the calorimetric experiment in no way differed from that used above. The experimental results are set forth in Table 2.

Our experimental values agree within the limits of accuracy of our work (± 0,6%) with those of previous investigations of these materials by Giauque and Archibald [10] (36,490 cal/mole for the same dilutions). Mention may also be made of Alentyev's paper [11] which described a method of evaluation of natural carbonates.

From the known heat of the reaction

$$MgO_{(solid)} + 2HCl_{(1:55)} = MgCl_{2\ (1:2000)} + H_2O_{(liq.)} + 36320 \pm 230 \text{ cal.}, \quad (5)$$

we can obtain, by summation of this equation with equation (1), the heat of the reaction:

$$MgCO_3\ (solid) = MgO_{(solid)} + CO_{2(gas)} + 23520 \text{ cal.} \quad (6)$$

A similar calculation for the heat of dissociation of $BaCO_3$, taking into consideration the literature values for $\Delta H°CO_2$ and $\Delta H°BaO$ [14] gives:

$$BaCO_3\ (solid) = BaO_{(solid)} + CO_2\ (gas) + 61000 \text{ cal.} \quad (7)$$

These constants are included in Table 3.

TABLE 2

Heat of Solution of Magnesium Oxide in 1 M HCl at 25°

Wt. of MgO in g	Wt. of HCl in g	Δt_1 (dissolution of oxide)	Correction for radiation, in %	Δt_2 (determination of thermal equivalent of system)	Correction for radiation, in %	Thermal equivalent of system in cal/deg.	Heat of solution of MgO, in cal/mole
0,3814	401,15	0,812	1,03	0,778	4,9	422,8	36320
0,4029	400,02	0,861	0,36	0,799	1,17	422,5	36410
0,3920	400,07	0,847	2,8	0,754	5,6	419,7	36560
0,3880	400,06	0,828	0,24	0,769	2,3	420,6	36190
0,4027	403,51	0,884	1,5	0,808	3,8	427,6	36140
			Mean 36320 ± 230 cal (± 0,6)				

TABLE 3

Heats of Formation ($-\Delta H^\circ_{298}$) and Dissociation (q) of Carbonates of the Second Group at 25° in kcal

(A) $Me_{(solid)} + C_{(graphite)} + {}^3/_2 O_{2(gas)} = MeCO_3$ (solid)

Carbonate	($BeCO_3$)	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$	($RaCO_3$)
$-\Delta H^\circ_{298}$	(243)	260,4	283,5	290,5	288	(300)

(B) $MeO_{(solid)} + CO_2$ (gas) = $MeCO_3$ (solid)

q	(5,6)	23,5	42,5	55,7	61,0	(72)

4. Results of Investgation of Thermal Dissociation

In this paper we have already put forward a number of considerations supplementing our previously published results on the investigation of the thermal dissociation of beryllium carbonate [3]. In the latter we assumed, on the basis of earlier data, ΔH° BeO = 135 kcal. Recently Cosgrove and Snyder [12] determined the heat of formation of BeO by a direct method to an accuracy ± 0,1 kcal. With the aid of this value (143.3 kcal) and the heat of formation of CO_2 (94,030 kcal), we obtain according to our experimental data [3]:

$$Be_{(solid)} + C_{(graph.)} + {}^3/_2 O_2(gas) = BeCO_3(solid).\ \Delta H^\circ_{BeCO_3} = -243\ kcal/mole. \qquad (8)$$

Our evaluation involves extrapolation since $BeCO_3$ can exist in the pure form only at above the standard temperature. These values are therefore put in brackets in Tables 3 and 4.

Closer consideration must be given to the dissociation equilibrium of strontium carbonate. After our paper [5] had been published, Lander [15] examined the same system and did not report any new data in connection with thermal dissociation. For the first time, however, Lander investigated the heat capacity of strontium carbonate:

$$C_p = 21,41 + 8,56 \cdot 10^{-3}\ T - 3,396 \cdot 10^5\ T^{-2}$$

The values of the Σ-functions [16,17], calculated with the help of the above equation, and our earlier data for P_{CO_2}, diverge somewhat (for example Σ = 13,0 [5] and Σ = 15,6 [15] for 850°), but in practice this difference has little effect upon the final value of ΔF_{298} and ΔH_{298}. The results of Lander substantially confirm our results.

Consequently, the values $\Delta H_0 = -53885$ cal and I = 32,06 cal/mole. deg, and the values of the Σ-functions obtained by our method [5] can be directly utilized for calculation of ΔF_{298}. We preferred, however, in the first place to try out one more method of calculation of ΔH_0 and I, using the standard entropies of the reactants [13]. In this case we obtain $\Delta H_0 = -58125$ cal, I = 35,60 cal/mole. deg. Without showing preference either for the first or the second method, and taking a mean value, we find $\Delta H_0 = -56{,}000$ cal; I = 33,83 cal/mole. deg, which on substitution in the usual equations for dependence of ΔF and ΔH on temperature gives for standard conditions $\Delta F_{298} = -43{,}520$ and $\Delta H_{298} = -55710$.

The values obtained, which we calculated from investigations of the equilibrium at high temperatures, are in satisfactory agreement with those previously found by the calorimetric method ($\Delta F_{298} = -43{,}900$ cal and $\Delta H_{298} = -56{,}100$ cal [4]). Consequently, we may assume as a basis for the dissociation of strontium carbonate

$$SrCO_3\ (solid) = SrO\ (solid) + CO_2(gas) - 56.1 \pm 0.4\ (\pm 1\%) \quad (9)$$

Introducing the heats of formation of SrO and CO_2 [13], we get

$$Sr(solid) + C(grapn.) + {}^3/_2\ O_2(gas) = SrCO_3\ (solid) - 290.5\ kcal/mole. \quad (10)$$

The foregoing considerations permit a generalization of the thermochemical data for the carbonates (Table 3) both for standard heats of formation (A) and for heats of dissociation (B). Data are also included for calcite from a critical survey of the thermal constants in 1949 [13]. The bracketed values are extrapolated results for radium (see theoretical part below) and for beryllium (see preceding section).

THEORETICAL

The experimental data for the thermochemistry of carbonates of metals of the second group in conjunction with literature data enable the establishment of a series of thermodynamic and crystallochemical constants not only for the carbonates themselves but also for the cations entering into their composition as well as for the carbonate ion.

1. Standard Free Energies of Thermal Dissociation of Carbonates

For the reaction $MeCO_3 \rightleftharpoons MeO + CO_2$ the values of ΔH_{298} that we found were given in Table 3 (B). Since

$$\Delta F_{298} = \Delta H_{298} - T\Delta S, \quad (11)$$

the calculation of ΔF_{298} requires the value of the entropies of MeO, $MeCO_3$ and CO_2. These values appear in Kelley's survey [18], while the unmeasured value of S for $BeCO_3$ could be evaluated by Kireev's method [19]. In view of the instability of the pure carbonate and the uncertainty in the accuracy of the evaluations, the corresponding values of the constants for $BeCO_3$ are enclosed in brackets. In the following Table 4 is given our extrapolated value of ΔF_{298} for $RaCO_3$, whose accuracy is $\pm$ 4%.

TABLE 4

Standard Free Energies of Dissociation of Carbonates of the Second Group in kcal

Carbonate	($BeCO_3$)	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$	($RaCO_3$)
$-\Delta F_{298}$	(−6.7)	11.0	31.1	43.5	48.8	(49)

2. Properties of Ions in Solution

The solubility product (L_p) at 25° for $MgCO_3$ is one of the least known. For this substance we actually obtained reliable thermochemical data with whose help it is not difficult to calculate L_p. The free energy of solution of the carbonate in water (ΔF_{298}) is the sum of the free energies of the processes:

$$MeCO_3(solid) = Me(solid) + C(graph.) + {}^3/_2O_2(gas) \quad (12)$$

$$Me(solid) + aq = Me^{\cdot\cdot}\ (aq). \quad (13)$$

$$C(graph) + {}^3/_2O_2(gas) + aq = CO_3^{\cdot\cdot}\cdot aq. \quad (14)$$

The free energies of processes (13) and (14) are well-known [20]; concerning the energy of solution of process (12), this is found from equation (11) with the help of our data for $MgCO_3$ and the entropy of the reactants [13].

We then obtain:

$$L_p = 1.76 \cdot 10^{-5}\ (at\ 25°) \quad (15)$$

This constant is given by a rigorous method on the basis of reliable thermodynamic data. We may note that in Landolt-Börnstein [21] the value given is queried, while Seidel [22], gives it for the trihydrate of the carbonate under a CO_2 pressure of 1 atm.; Bolländer [23], like Landolt, gives it for 12°. Of these values ($1.2 \cdot 10^{-6}$; $1 \cdot 10^{-5}$; $2.6 \cdot 10^{-5}$) the first is known to be inaccurate, the second relates to the trihydrate, and the third is not at standard temperature. We may therefore recommend our estimated value as the only one relating to pure crystalline $MgCO_3$ in water at 25°

The entropy of the aqueous carbonate ion was found by Latimer, Pitzer and Smith [24] by studying the ionization of carbonic acid (− 13.0 ± 1.0 entropy unit). Since the dissociation equilibrium of carbonic acid in aqueous solution is a complex one, the accuracy of this value is doubtful. Moreover, we have at our disposal three simpler methods of establishing the entropy of the carbonate ion which are also independent of one another. Carrying out the summation for these three processes (12), (13) and (14) of the free energies and heats of reaction taken from our experimental data and from the literature [20, 25] we obtain from equation (11) the change of entropy during dissolution of $MgCO_3$ in water:

$$MgCO_3(solid) = Mg^{\cdot\cdot}\ (aq) + CO_3^{\cdot\cdot}(aq), \quad \Delta S_{298} = -58.25\ kcal/degree. \quad (16)$$

The entropy of $MgCO_3$(solid) was determined experimentally and found to be 15.7 ± 0.2 entropy units [13].

Since Latimer and co-workers [24] proposed two different values for the entropy of the magnesium ion, we calculated the S_{298} of the ion from our experimental data and found a value of −33.52 entropy units. Then from equation [16] we found for the carbonate ion in water: $S_{298} = -9.0$ entropy units. The considerable discrepancy between this value and that proposed by Latimer prompted us to repeat similar calculations starting from our own data for another carbonate ($BaCO_3$), which also gave a value of −9.0 entropy units. Since it might be feared that the calculations based on one and the same investigation are not sufficiently objective, we calculated the S_{298} of the carbonate ion from the data of Kapustinsky and Dezideryeva [4] for $SrCO_3$ and obtained $S_{298} = -9.1$ entropy units. Consequently one and the same value is obtained to an accuracy of 0.1 entropy unit by investigation of three different substances, so that we can regard the result of Latimer, Pitzer and Smith as inaccurate and we can propose for the entropy of CO_3'' aq the value $S_{298} = -9.0 \pm 0.1$ entropy units.

3. Crystallochemical Characteristics

By carrying out the Born-Haber cycle with utilization of our experimental values for the heats of formation of carbonates, we can obtain the energies of the crystal lattice of the carbonates (Table 5), and then, utilizing this value and the Goldschmidt radii of the cations, we can find from the equation of the energy of ionic lattices [26] the "thermochemical radius" of the carbonate ion. The last column of Table 5 shows the good constancy of this value, regardless of which of the carbonates we start from. The slight drop at the start of the group is explained by the effect, already described by one of us and Yatsimirsky [27], of introduction of a small cation into the interior of a non-spherical anion.

Table 5

"Thermochemical Radius" of the Carbonate Ion

Compound	Radius of cation, in A	Lattice energy from the Born-Haber cycle	Radius of CO_3''
$BeCO_3$	0.34	905	1.79
$MgCO_3$	0.78	770	1.82
$CaCO_3$	1.06	689	1.86
$SrCO_3$	1.27	657	1.84
$BaCO_3$	1.43	629	1.85

The mean value of the "thermochemical radius" of CO_3'' is r = 1.83 ± 0.02 A. This value agrees to within 0.5% with that calculated by Yatsimirsky [25].

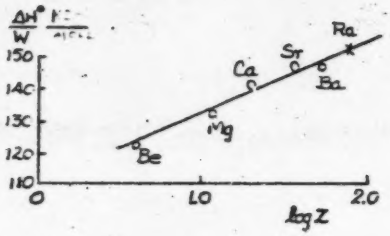

Fig. 5.

The energy of the crystal lattice (u) can also be represented as the square of the difference of the "crystallochemical electronegativities" of the cation $\kappa_{C^{\cdot\cdot}}$ and the anion $\kappa_{A^{\cdot}}$ [28]:

$$u = \Sigma(\kappa_{C^{\cdot\cdot}} - \kappa_{A^{\cdot}})^2, \qquad (17)$$

where Σ is the sum of the bonds. For cations of the 2nd group, the values of κ are known [28]. Substituting in the above formula the experimental lattice energies (Table 5) we find that value of κ for CO_3'' ion which best corresponds to the already known $\kappa_{C^{\cdot\cdot}}$.

In order to check the found $\kappa_{CO_3''} = 0.2$, it may be substituted in equation (17) and with the help of Table 5 we may calculate $\kappa_{C^{\cdot\cdot}}$; the values of the latter are found to agree to within 2% with the values previously assumed for all five cations.

4. The Rule of Thermochemical Logarithmicity

According to this rule [1], the heat of formation of compounds per gram-equivalent within each group for ions (atoms) of electronic analogs must be linearly dependent on the logarithm of the atomic number of the cation (log Z_C). This generalization, which establishes a link between thermochemistry and Mendeleev's periodic law and which is based on the concept of the electronic structure of the atom, makes provision for the possibility of deviation from linear dependence for $Be^{\cdot\cdot}$, as a two-electron ion in contrast to the ions with an 8-electron configuration which follow it. Whether, however, this deviation was considerable or minute could not previously be estimated since this

depends upon the nature of the ion. Figure 5, in which are plotted the heats of formation per gram-equivalent ($\Delta H/W$) as a function of the logarithm of $Z_{C^{--}_3}$, shows that this deviation is so insignificant that it nearly coincides with the attainable margin of error. The rule of thermochemical logarithmicity is well confirmed by the experimental material for the thermochemistry of elements of the 2nd group, and we are therefore justified in graphically extrapolating the straight-line plot in order to ascertain the heat of formation of radium carbonate: for the latter we get $H^{\circ}_{298} = -300$ kcal.

SUMMARY

1. An investigation of the heats of solution of magnesium and barium in acid and a study of the thermal dissociation of the carbonates of beryllium ($BeCO_3 \cdot BeO$) and strontium has given the standard heats of formation and also the heats and free energies of thermal dissociation of the carbonates of Be, Mg, Sr and Ba (Tables 3 and 4).

2. With the help of the foregoing data and of the thermodynamic constants critically selected from the literature, calculations were made of the solubility product of $MgCO_3$ $L_p = 1.76 \cdot 10^{-5}$ at 25° and of the entropy of the carbonate ion (CO_3^{--}) $S_{298} = -9.0 \pm 0.1$ entropy units.

3. On the basis of the thermochemical data obtained and with the help of the calculated energy of the crystal lattice, values are found for the "thermochemical radius" of the CO_3^{--} ion $r = 1.83 \pm 0.02$ A, and of the "crystallochemical electronegativity" of CO_3^{--} $\kappa = 0.2$. Both of these magnitudes are in complete agreement with the experimental data for all the five above-mentioned carbonates.

4. Confirmation is obtained of the applicability of the rule of thermochemical logarithmicity to carbonates of elements of the second (main) group of the periodic system of Mendeleev. Extrapolation with the aid of this law gives for the heat of formation of radium carbonate a value of $\Delta H^{\circ}_{298} = -300$ kcal/mole.

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SYSTEMS CONTAINING CONCENTRATED HYDROGEN PEROXIDE

V. THERMAL CHARACTERISTICS OF THE SOLID PHASES OF THE SYSTEM $Ca(OH)_2 - H_2O_2 - H_2O$

S. Z. Makarov and N. K. Grigoryeva

In a study of the system $Ca(OH)_2 - H_2O_2 - H_2O$ over the temperature range of 0 to -21°, it was established [1] that the products of interaction of calcium hydroxide with hydrogen peroxide are undoubtedly the three solid phases: $CaO_2 \cdot 8H_2O$, $CaO_2 \cdot 2H_2O$ and $CaO_2 \cdot 2H_2O_2$.

In order to supplement the method of analytical examination, which was inadequate for full physicochemical characterization of the solid phases of the system, use was made of the methods of thermal analysis and X-ray examination; photomicrographs were also taken and a study was made of the thermal stability and of the processes of dehydration of the hydrated forms of calcium peroxide. The prepared peroxy compounds of calcium, also the anhydrous calcium peroxide and calcium hydroxide, were subjected to thermal anaylsis with the differential recorder, using a recording pyrometer of the Kurnakov type.

The heating curve of anhydrous calcium peroxide CaO_2 (Fig.1) is characterized by the presence of one endothermic effect corresponding to the breakdown of CaO_2 to CaO with evolution of active oxygen. Since the reaction of formation of CaO_2 is accompanied by heat evolution, an endothermic course of the decomposition reaction is entirely probable. Calcium peroxide contains 21.0% active oxygen.

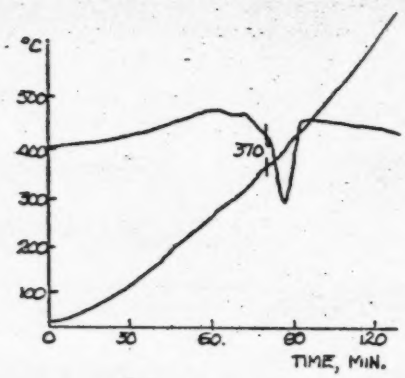

Fig. 1. Heating curve of CaO_2.

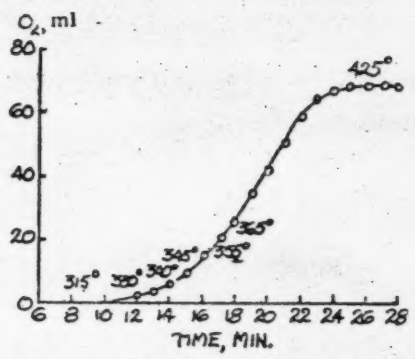

Fig. 2. Thermal stability of CaO_2 (check by amount of oxygen released)

For more accurate characterization of the thermal stability of CaO_2, observations were made, parallel with the recording of the heating curve, of the evolution of active oxygen. For this purpose, the vessel in which the heating was carried out was connected to a measuring buret containing water saturated with oxygen, and at definite intervals of time measurements were made of the volume of evolved gas as well as of the corresponding temperatures. Data for the measurements are set forth in Table 1 and plotted in Fig. 2.

The process of thermal decomposition was also checked from the determination of the content of active oxygen in the residue after heating of CaO_2 to a definite temperature at a heating velocity of 4-5° per min. (Table 2 and Fig. 3).

Table 1

Duration in min.	Temp. °C	Amount of oxygen evolved, in ml	Duration in min.	Temp. °C	Amount of oxygen evolved in ml
68	315	0.8	81	-	51.0
71	330	2.4	82	-	59.4
73	340	4.2	83	-	65.6
74	345	7.2	84	-	68.0
76	355	16.0	85	425	69.0
78	365	26.0	86	-	69.0
79	-	35.0	89	-	69.0
80	-	43.0	90	-	69.0

Table 2

Heating temp. in °C	Amount of active oxygen evolved, in %	Heating temp. in °C	Amount of active oxygen evolved in %
175	0.15	340	1.58
200	0.23	360	5.20
250	0.60	380	13.75
300	0.90	400	18.0
320	1.15	425	19.6

We see that up to 175° anhydrous calcium peroxide CaO_2 is completely stable; from 175 to 300° there is insignificant loss of active oxygen (approx. 0.9%), and only above 300° does intensive breakdown of CaO_2 take place as reflected by the corresponding thermal effect on the heating curve. Complete decomposition of CaO_2 is completed at 400-425°.

The heating curve of calcium peroxide dihydrate $CaO_2 \cdot 2H_2O$ (Fig. 4) has two endothermic effects: the first at 100° corresponds to dehydration of $CaO_2 \cdot 2H_2O$ with transformation into CaO_2 containing 18-19% active oxygen, while the second starts at above 300° and is complete at 400-425°, corresponding to the decomposition of anhydrous calcium peroxide into CaO (in analogy with Fig. 1).

The heating curve of calcium peroxide octahydrate $CaO_2 \cdot 8H_2O$ (Fig. 5) has three endothermic effects, the first two of which are associated with a two-stage dehydration. At 40° the octahydrate melts in its water of crystallization and splits off 6 molecules of H_2O to form $CaO_2 \cdot 2H_2O$. The second effect at 100° corresponds to the process of removal of the two last molecules of water and transformation into anhydrous calcium peroxide (see also Fig. 4). The third effect, as in the preceding curves for CaO_2 and $CaO_2 \cdot 2H_2O$, corresponds to the decomposition of CaO_2. The heating curve clearly shows that the thermal effect of removal of six molecules of water is considerably less than that of the two last molecules. The implication is that the two last molecules of water in calcium peroxide octahydrate are very much more firmly bound than the first six molecules.

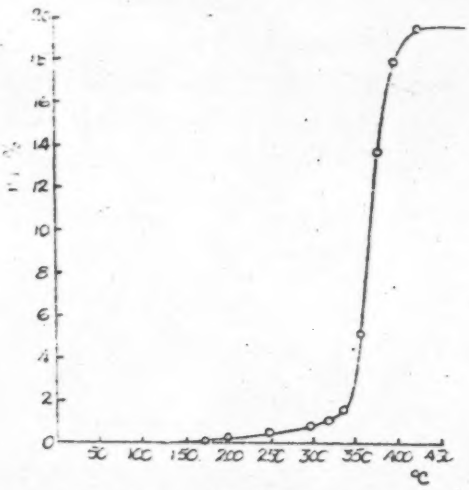

Fig. 3. Thermal stability of CaO_2 (check by oxygen content of residue).

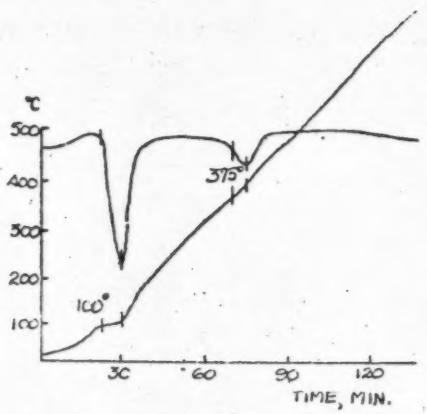

Fig. 4. Heating curve of $CaO_2 \cdot 2H_2O$.

The heating curves of $CaO_2 \cdot 8H_2O$ and $CaO_2 \cdot 2H_2O$ show that the two-stage successive dehydration of $CaO_2 \cdot 8H_2O$ proceeds with a like thermal effect, whereas de Forcrand [2], in examining the two stages of successive hydration of CaO_2 to $CaO_2 \cdot 2H_2O$ and to $CaO_2 \cdot 8H_2O$, observed unlike thermal effects, namely, he established that the binding of the first two molecules of H_2O to solid CaO_2 proceeds with absorption of –2.215 cal, while the addition of the six molecules of water proceeds with evolution of + 17.851 cal. On this basis he concluded that $CaO_2 \cdot 2H_2O$ is not a true hydrate of calcium peroxide but a combination of H_2O_2 with hydrated lime $Ca(OH)_2 \cdot H_2O_2$, which thus also accounts for the difference in properties. This theory was supported by Foregger and Philipp [3].

However, our plot of the heating curve of $CaO_2 \cdot 2H_2O$ conclusively points to a hydrated compound of calcium peroxide with an endothermic effect of dehydration. The presence of a molecule of H_2O_2 would have given an exothermic effect on the heating curve due to the evolution of active oxygen as is usually observed with perhydrates of peroxides.

The heating curve of the diperhydrate of calcium peroxide $CaO_2 \cdot 2H_2O_2$ (Fig. 6) is characterized by one exothermic effect and two endothermic effects. The specimen of $CaO_2 \cdot 2H_2O_2$ contained 31% active oxygen. This very oxygen-rich peroxy compound of calcium theoretically contains 34.4% active oxygen.

The exothermic effect at 40–45° is the result of evolution of active oxygen from the combined hydrogen peroxide, with transformation of the $CaO_2 \cdot 2H_2O_2$ into $CaO_2 \cdot 2H_2O$ according to the reaction: $CaO_2 \cdot 2H_2O_2 \rightarrow CaO_2 \cdot 2H_2O + O_2$.

At this point it is pertinent to mention that the direction of this reaction is associated with the evolution of active oxygen and not with the transformation of $CaO_2 \cdot 2H_2O_2$ into $CaO_2 \cdot 2H_2O$. Later an endothermic effect is observed which corresponds to dehydration and transformation into CaO_2, and, finally, the last effect is bound up with the breakdown of CaO_2 to CaO.

Simultaneously with the recording of the heating curve of $CaO_2 \cdot 2H_2O_2$, a study was made of the process of its thermal decomposition which was checked by the evolution of active oxygen. The results are set forth in Table 3 and the decomposition curve is shown in Fig. 7.

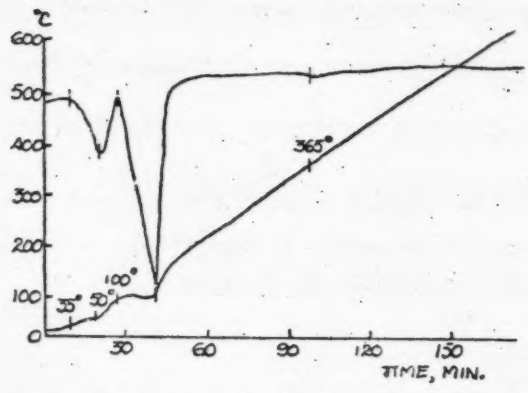

Fig. 5. Heating curve of $CaO_2 \cdot 8H_2O$

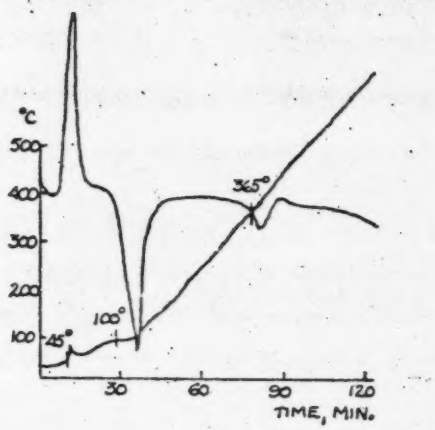

Fig. 6. Heating curve of $CaO_2 \cdot 2H_2O_2$

Table 3

Period, in min.	Temp., in °C	Amount of oxygen, in ml	Period, in min.	Temp., in °C	Amount of oxygen, in ml	Period, in min.	Temp., in °C	Amount of oxygen, in ml
16	48	0.2	23	70	102.0	96	–	111.0
17	51	1.0	30	95	102.0	98	–	115.0
18	54	3.0	87	335	102.2	100	–	118.0
19	57	5.0	88	340	103.0	102	–	122.0
20	60	12.0	90	350	104.0	104	400	124.0
21	63	30.0	92	–	106.0	106	–	124.2
22	65	97.0	94	–	108.0	108	–	124.2

The data show that the process of thermal decomposition of $CaO_2 \cdot 2H_2O_2$ to $CaO_2 \cdot 2H_2O$ proceeds exceptionally rapidly with great evolution of heat; at above 300° complete decomposition of calcium peroxide takes place. For the purpose of comparison the heating curve of calcium hydroxide $Ca(OH)_2$ was plotted (Fig. 8); this has one endothermic effect at 530-540°, corresponding to a dissociation different from that previously described.

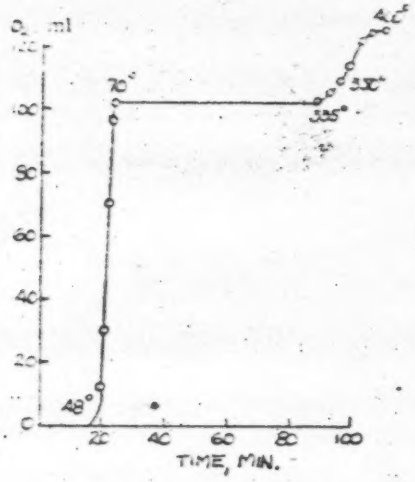

Fig. 7. Thermal decomposition of $CaO_2 \cdot 2H_2O_2$ (check by evolution of oxygen).

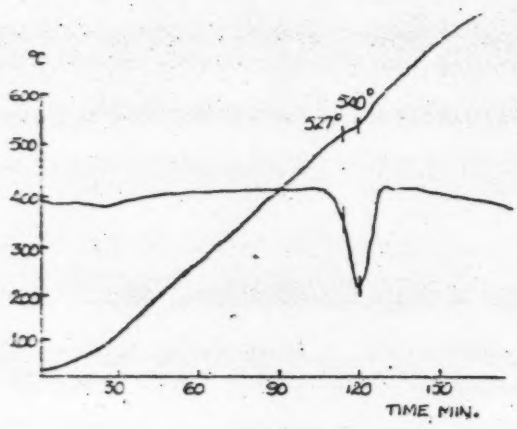

Fig. 8 Heating curve of $Ca(OH)_2$.

According to recent data of Shinemann and King [4] on the structure of $CaO_2 \cdot 8H_2O$, the crystals of this compound belong to the tetragonal system. This is confirmed by photomicrographs and X-ray data obtained in the Laboratory of Peroxy Compounds of the Acad. Sci. USSR. $CaO_2 \cdot 8H_2O$ is a stable compound at a temperature of 35-40° if kept in hermetically sealed vessels; in the air it is readily carbonated. It easily gives up its water of crystallization in presence of dehydrating agents and on heating. Calcium peroxide dihydrate is a reddish powder, stable up to 100°. Anhydrous calcium peroxide is a very fine, cream-colored powder, stable up to 300°

Calcium peroxide diperhydrate $CaO_2 \cdot 2H_2O_2$, with a very wide region of existence in equilibrium with the liquid phase over a wide range of concentrations of hydrogen peroxides and temperatures, is unstable in the free state and gradually breaks down to $CaO_2 \cdot 2H_2O$ with loss of active oxygen from the peroxide group. It slowly decomposes at low temperatures.

SUMMARY

1. Thermal analysis confirmed that all the three solid phases which were detected in the study of the isotherms of the system $Ca(OH)_2 - H_2O_2 - H_2O$ in the temperature range of -21 to 0° are actually individual peroxy compounds of calcium.

2. The octahydrate $CaO_2 \cdot 8H_2O$ and the dihydrate $CaO_2 \cdot 2H_2O$ of calcium peroxide are readily dehydrated and are converted into anhydrous calcium peroxide which is stable up to 300°

3. The diperhydrate of calcium peroxide $CaO_2 \cdot 2H_2O_2$, which exists over a wide region in equilibrium with the liquid phase, is unstable in the free state and readily breaks down with formation of $CaO_2 \cdot 2H_2O$.

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THE ALLYL REARRANGEMENT IN THE POLYCHLOROBUTENOIC ACID SERIES AND SOME ERRORS BY AUWERS AND WISSEBACH IN THEIR PAPERS [1,2]

A. N. Nesmeyanov, L. I. Zakharkin, V. N. Kost and R. Kh. Freidlina

In the previous communication [3] we showed that although trichloropropenes with the structure $CCl_3CH = CH_2$ and $CCl_2 = CH-CH_2Cl$ do not exist in a state of reciprocal isomerization equilibrium, in a large number of exchange reactions they nevertheless form one and the same products with the structure $CCl_2=CH-CH_2X$, where X is a nucleophilic group exchanging with halogen, regardless of which of the two trichloropropenes is brought into reaction. This is true of the reactions of both trichloropropenes with diethylamine, sodium ethyoxide, sodium sulfide, sodium acetate, sodium malonic ester, copper cyanide, organomagnesium compounds, etc. In the course of these reactions 1,1,1-trichloropropene undergoes an anionotropic allyl rearrangement. We regard the exchange reactions of 1,1,1-trichloropropene as involving the mechanism of "transfer of the reaction center" [4] at the system of δ,π-conjugated bonds in accordance with schemes (1) and (2):

$$Cl-CCl_2-CH=CH_2 + \overset{\ominus}{X} \rightarrow Cl^{\ominus} + CCl_2=CH-CH_2X \qquad (1)$$

$$CCl_3-CH=CH_2 + \dot{X}_1 \rightarrow CCl_3-\dot{C}H-CH_2X_1 \rightarrow CCl_2=CH-CH_2X_1 + \dot{Cl} \qquad (2)$$

(compare with [5]).

In the present research we have studied the reciprocal relations of acids with the structure $CHCl_2-CH=CH-CO_2H$ and $CCl_2=CH-CH_2CO_2H$ and the corresponding behavior of their derivatives — involving a prototropic allylic rearrangement. In the literature are described two γ,γ-dichlorocrotonic acids. A γ,γ-dichlorocrotonic acid with m.p. 42-43° was obtained by Auwers and Wissebach [1,2] by reducing γ,γ,γ-trichlorocrotonic acid (see also [6]). A γ,γ-dichlorocrotonic acid with m.p. 101-102° was obtained from dichloroacetaldehyde and malonic acid [7].

We decided to prepare the previously unknown γ,γ-dichlorovinylacetic acid* by mild hydrolysis of its nitrile which we previously prepared [3] by the action of copper cyanide on 1,1,3-trichloropropene - 1:

$$CCl_2=CH-CH_2Cl + CuCN - CCl_2=CH-CH_2CN \xrightarrow[H^+]{H_2O} CCl_2=CH-CH_2-COOH$$

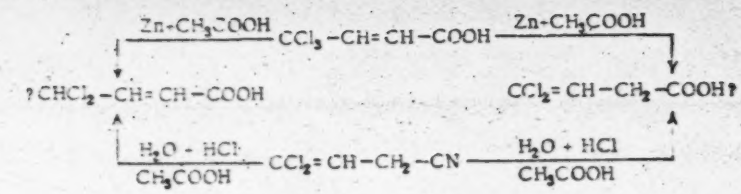
The γ,γ-dichlorovinylacetic acid that we synthesized melts at 42-43°, the same as the acid described by Auwers and Wissebach as γ,γ-dichlorocrotonic acid. Determination of the melting point of a mixed specimen of our acid and the acid obtained by the method of Auwers and Wissebach did not give a depression. The products of addition of chlorine and bromine to the acids synthesized by both methods also were identical products, as confirmed by the absence of depression of the melting point in mixed tests.

In support of the view that the acid obtained by both methods has the structure of γ,γ-dichlorovinylacetic acid, we may point out that, according to the data of Auwers and Wissebach, its esters do not exhibit an exaltation of molecular refraction, while its hydrolysis in presence of conc. H_2SO_4 leads to succinic acid. Opposing this view, on the other hand, is the reduction by the cited authors of the acid under the action of sodium amalgam to form crotonic acid. The problem is further complicated by the fact that Auwers and Wissebach [2], starting from the acid synthesized by them, obtained a nitrile via the chloride and amide; in its constants this nitrile differed from the nitrile of γ,γ-dichlorovinylacetic acid and exhibits an exaltation of molecular refraction. Repetition of the synthesis of these derivatives by the procedure of the cited authors, starting from specimens of acids prepared by both routes, led to one and the same acid chloride, amide, and nitrile regardless of the origin of the starting acid. However, only the constants of the acid chloride fully agreed with those described, whereas the constants of the amide and nitrile differed.

Since the structure of the starting substances for the synthesis of the unsaturated dichloro acid by both methods has been conclusively established (the structure of γ,γ,γ-trichlorocrotonic acid was established by its acid hydrolysis to fumaric acid; that of the nitrile of γ,γ-dichlorovinylacetic acid by acid hydrolysis to succinic acid), we must assume that one and the same acid could only be obtained as the result of rearrangement either in the process of reduction of the trichlorocrotonic acid or in the process of hydrolysis of the nitrile in question, as we see from the

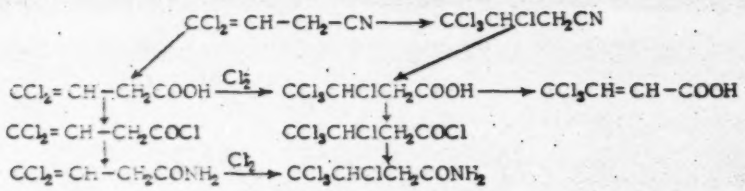
* Vinylacetic acid = 3-butenoic acid. Publisher.

following scheme:



We arrived at a solution of this problem on the basis of the following considerations. On the one hand, the addition of chlorine to the nitrile of γ,γ-dichlorovinylacetic acid gave the nitrile of β,χ γ,γ-tetrachlorobutyric acid from which the corresponding acid, the chloride and the amide, were then obtained by the usual method. Isomerization is very improbable in the first stage of this chain of transformations, while in the remaining stages it is obviously excluded. The structure of β, γ,γ,γ,-tetrachlorobutyric acid was proved by its dehydrochlorination to γ,γ,γ-trichlorocrotonic acid, identical with that described by Auwers and Wissebach and unambiguous in structure, so that the possibility of isomerization during the first stage is also excluded.

On the other hand, the investigated dichloro acid obtained by acid hydrolysis of the nitrile of γ,γ-dichlorovinylacetic acid was transformed by the usual routes into chloride, amide and nitrile (the latter proved to be identical with the starting nitrile). Addition of chlorine to this acid, its amide and nitrile led to formation of compounds identical with the above-described β, γ,γ,γ-tetrachlorobutyric acid and its derivatives. These results are summarized in the scheme:



These data show that the above-mentioned acid has the structure of γ,γ,-dichlorovinylacetic acid and that isomerization does not take place in the course of its preparation from the nitrile and in the course of its transformations in the conditions described in the experimental part. Consequently, on reduction of γ,γ,γ,-trichlorocrotonic acid under the action of zinc and glacial acetic acid in ethyl alcohol, there is formed not γ,γ,-dichlorocrotonic acid, as Auwers and Wissebach believed, but γ,γ-dichlorovinylacetic acid, i.e. the reduction takes place with rearrangement:

$$CCl_3-CH=CH-COOH \xrightarrow[CH_3COOH]{Zn} CCl_2=CH-CH_2-COOH.$$

Dichlorovinylacetic acid is incapable of further reduction in the same conditions [1].

We also succeeded in explaining the fact, at first inexplicable, that γ,γ-dichlorovinylacetic acid is reduced to crotonic acid with the help of sodium amalgam [1]. We found that γ,γ-dichlorovinylacetic acid, its amide and nitrile are easily isomerized under the action of a base (e.g triethylamine) to γ,γ-dichlorocrotonic acid and its derivatives. The obtained γ,γ-dichlorocrotonic acid proved to be identical with the acid synthesized from dichloroacetaldehyde and malonic acid [7], which fact confirmed its structure. Since the reduction of γ,γ-dichlorovinylacetic acid by Auwers and Wissebach was effected under the action of sodium amalgam, conditions were created for its isomerization to γ,γ-dichlorocrotonic acid and for its further reduction to crotonic acid.

The tranformation of γ,γ,γ-trichlorocrotonic acid, on the one hand, by hydrolysis to fumaric acid, and, on the other hand, by reduction to crotonic acid is cited in modern monographs on stereochemistry and in textbooks of organic chemistry as a strict proof of the trans-structure of crotonic acid and as an example of the establishment of the geometrical configuration by transformation into a derivative of known configuration by reactions which leave intact the olefinic carbon linkages. Now we see that the two-stage reduction of γ,γ,γ-trichlorocrotonic acid to crotonic acid, which was carried out by Auwers and Wissebach, proceeds with a twofold isomerization which was not observed by the authors, and therefore it cannot serve to establish the configuration of crotonic acid. We also see that the allylic rearrangement introduces substantial limitations into the method of establishment of the configuration based on transformation into a derivative with a known spatial structure.

Our preparations of acid chloride amides and nitriles of both γ,γ-dichlorovinylacetic acid and of γ,γ-dichlorocrotonic acid permitted us to establish that the acid chloride described by Auwers and Wissebach is the chloride of γ,γ-dichlorovinylacetic acid, while the amide and nitrile described by them are derivatives of γ,γ-dichlorocrotonic acid. It is evident that in the process of transformation of γ,γ-dichlorovinylacetyl chloride into an amide an

isomerization not detected by the authors took place with formation of the amide of γ,γ-dichlorocrotonic acid.

It should be noted that neither of the series of the derivatives studied of the type of $CCl_2=CH-CH_2X$ and $CHCl_2CH=CH-X$ isomerizes in an acid medium. Thus, on hydrolysis of the nitrile of γ,γ-dichlorovinylacetic acid in a mixture of hydrochloric and acetic acids, γ,γ-dichlorovinylacetic acid was obtained, while hydrolysis of γ,γ-dichlorocrotonitrile in the same conditions gave γ,γ-dichlorocrotonic acid. The same must be said about γ,γ,γ-trichlorocrotonic acid, which hydrolyzes without isomerization in a strongly acidic medium with formation of fumaric acid. Hence it follows that the preparation by Auwers and Wissebach of γ,γ-dichlorovinylacetic acid on reduction of γ,γ,γ-trichlorocrotonic acid in an acid medium cannot be explained either by preliminary isomerization of the starting acid or by the hypothesis of intermediate formation of γ,γ-dichlorocrotonic acid followed by the latter's isomerization. It is evident that the rearrangement takes place in the very process of reduction. We suggest that this reaction also proceeds according to the mechanism of "transfer of the reaction center" as follows:

$$CCl_2-CH=CH-COOH + H \rightarrow CCl_2\dot{C}HCH_2COOH \rightarrow CCl_2=CH-\dot{C}H_2-COOH + Cl.$$

EXPERIMENTAL

Saponification of γ,γ-dichlorovinylacetonitrile. γ,γ-Dichlorovinylacetonitrile was prepared by the action of copper cyanide on 1,1,3-trichloropropene-1 [2]. A solution of 35 g γ,γ-dichlorovinylacetonitrile in 65 ml glacial acetic acid, 30 ml conc. HCl and 30 ml water was boiled for 5 hours. After cooling, water was added and the product extracted with chloroform. The solvent was driven off and the residue distilled in vacuum. B.p. of γ,γ-dichlorovinylacetic acid 111-112° (7mm); m.p. 42-43° (from ligroine); yield 38 g (95% of theory).

	Found %	C 31.22; 31.26;	H 2.70; 2.63
$C_4H_4O_2Cl_2$.	Calculated %	C 31.01	H 2.57

The acid does not give a melting point depression in a mixed test with the acid obtained by reduction of γ,γ,γ-trichlorocrotonic acid [1,2].

β,γ-Dibromo-γ,γ-dichlorobutyric acid is obtained in quantitative yield by addition of bromine to γ,γ-dichlorovinylacetic acid under irradiation: m.p. 121-122°. The acid does not give a melting point depression with the dibromodichlorobutyric acid prepared by addition of bromine to the acid formed by reduction of γ,γ,γ-trichlorocrotonic acid [1,2].

β,γ,γ,γ-Tetrachlorobutyric acid is obtained in quantitative yield by addition of chlorine to γ,γ-dichlorovinylacetic acid in chloroform solution under irradiation: m.p. 108-109°.

	Found %	C 21.42; 21.66;	H 1.56; 1.61
$C_4H_4O_2Cl_4$.	Calculated %	C 21.24;	H 1.76

The acid does not give a melting point depression in a mixed test with the acid obtained by saponification of γ,γ,γ-tetrachlorobutyronitrile.

Saponification of β,γ,γ,γ-tetrachlorobutyronitrile. β,γ,γ,γ-Tetrachlorobutyronitrile was obtained by addition of chlorine to γ,γ-dichlorovinylacetonitrile in chloroform solution under irradiation [3]. A solution of 8 g β,γ,γ,γ-tetrachlorobutyronitrile in 20 ml acetic acid, 10 ml conc. HCl and 10 ml water was boiled for 8 hours. After cooling, water was added and the product extracted with chloroform. The solvent was driven off and the solid residue recrystallized from a mixture of benzene and ligroine; m.p. 108-109°; yield 7.9 g (91% of theory).

Dehydrochlorination of β,γ,γ,γ-tetrachlorobutyric acid. 6.8 g β,γ,γ,γ-tetrachlorobutyric acid was dissolved in an aqueous solution of NaOH (3 g NaOH in 25 ml water) and the solution stood at room temperature for 5 hours. The solution was then acidified with hydrochloric acid and extracted with ether. The ethereal extract was dried with calcium chloride. After driving off the ether, the solid residue was recrystallized from ligroine, m.p. 113-114°; yield 3.8 g (67% of theory). The acid obtained does not give a depression of m.p. in a mixed test with an authentic specimen of γ,γ,γ-trichlorocrotonic acid.

β,γ,γ,γ-Tetrachlorobutyrylchloride is prepared in quantitative yield by 4 hours' boiling of β,γ,γ,γ-tetrachlorobutyric acid with twice the weight of thionyl chloride. The chloride has b.p. 69-70° (2.5 mm); n_D^{28} 1.5130; d_4^{20} 1.6129; found MR 45.53; Calculated for $C_4H_3Cl_5O$ MR 45.39.

β,γ,γ,γ-Tetrachlorobutyramide was obtained by saturating an ethereal solution of the chloride with ammonia at 0°. After the ether had been driven off, the crystalline residue was extracted with hot benzene. On cooling the benzene deposits the amide which after recrystallization has m.p. 138-138.5°.

Found %: N 6.18; 6.23

$C_4H_3NCl_4O$. Calculated %: N 6.22

γ,γ-Dichlorovinylacetyl chloride. A solution of 20 g γ,γ-dichlorovinylacetic acid in 80 g thionyl chloride was heated 4 hours on a water bath. The excess of thionyl chloride was driven off and the residue distilled in vacuum. Yield 21 g (85% of theory) of γ,γ-dichlorovinylacetyl chloride with b.p. 67-68° (13 mm); n_D^{20} 1.4995.

γ,γ-Dichlorovinylacetamide. Into a cooled solution of 20 g γ,γ-dichlorovinylacetyl chloride in 75 ml absolute ether was passed dry ammonia until saturated. After the ether had been driven off, the crystalline residue was extracted several times with hot benzene. On cooling, the benzene solution deposited the amide in the form of plates; m.p. 93-94° (from benzene); yield 16 g (90% of theory).

Found %: N 9.02; 9.15

$C_4H_5ONCl_2$. Calculated %: N 9.09

The amide does not give a depression of melting point in admixture with the amide prepared by the same route from the acid of Auwers and Wissebach.

Addition of chlorine led to a quantitative yield of β,γ,γ,γ-tetrachlorobutyramide with m.p. 138°; it did not give a depression of melting point with a specimen of the β,γ,γ,γ-tetrachlorobutyramide prepared as described above from β,γ,γ,γ-tetrachlorobutyric acid.

Dehydration of γ,γ-dichlorovinylacetamide. A mixture of 10 g γ,γ-dichlorovinylacetamide and 14.5 g phosphorus pentoxide was heated in vacuum at 60° for an hour. The resultant nitrile was distilled off and had b.p. 57° (17 mm); n_D^{20} 1.4842; d_4^{20} 1.3148; found MR 29.60; calculated for $C_4H_3Cl_2N$ MR 29.76. These constants are in good agreement with those for γ,γ-dichlorovinylacetonitrile prepared by the action of copper cyanide on 1,1,3-trichloropropene-1 [3]. n_D^{20} 1.4842; d_4^{20} 1.3142; yield 7.5 g (85% of theory).

The identity between these two nitriles was established by adding chlorine to them, when one and the same β,γ,γ,γ-tetrachlorobutyronitrile was obtained with m.p. 44°. A mixed sample did not give a m.p. depression.

Isomerization of γ,γ-dichlorbvinylacetonitrile under the action of triethylamine. To 5 g of γ,γ-dichlorovinylacetonitrile was added 5 drops triethylamine. The mixture was stood at room temperature overnight. Distillation of the product gave 3 g γ,γ-dichlorocrotonitrile with b.p. 90-91 (18 mm); n_D^{20} 1.4970; d_4^{20} 1.3055; found MR 30.49; calculated for $C_4H_3Cl_2N$ MR 29.76. Auwers and Wissebach give [2]: n_D^{20} 1.4973; d_4^{20} 1.3049.

Hydrolysis of γ,γ-dichlorocrotonitrile. A solution of 2 g γ,γ-dichlorocrotonitrile in 5 ml acetic acid, 2 ml conc. HCl and 3 ml water was refluxed for 6 hours. After cooling, water was added and the product extracted with chloroform. The solvent was removed and the residue distilled in vacuum. The 140-145° (20 mm) fraction was collected. Yield 1.6 g crystalline product which after recrystallization from a mixture of benzene and ligroine had m.p. 99-100°. Yield 70% of theory.

Isomerization of γ,γ-dichlorovinylacetic acid. 3 g acid was heated with 2.1 g triethylamine on a water bath at 75-80° for 4 hours. At the commencement of heating the mass was liquid, but subsequently crystals gradually came down. After cooling, dilute hydrochloric acid was added to the reaction mass; the oil which settled out was extracted with chloroform. The solvent was driven off and the solid residue distilled in vacuum; b.p. 101-102° (4 mm). The acid crystallized in the condenser; yield 2.1 g (70% of theory); m.p. 99-100° (from benzene-ligroine).

The acid does not give a depression of melting point in admixture with the acid obtained by hydrolysis of γ,γ-dichlorocrotonitrile.

Isomerization of γ,γ-dichlorovinylacetamide. A solution of 0.6 g amide (m.p. 93-94°) in 10 ml benzene and 3 drops triethylamine was refluxed 4 hours. To the hot solution was added ligroine; on cooling the γ,γ-dichlorocrotonamide came down as needles; m.p. 81-82° (the amide described by Auwers and Wissebach melted at 82-83°) yield 0.5 g (83% of theory). The melting point of a mixture with the original amide was 58-60°.

SUMMARY

1. γ,γ-Dichlorovinylacetic acid was prepared by hydrolysis of its nitrile. The chloride and amide of the acid were prepared by the usual methods.

2. It was shown that, under the action of bases, γ,γ-dichlorovinylacetic acid and its amide and nitrile isomerize to γ,γ-dichlorocrotonic acid and its amide and nitrile.

3. Both series of derivatives of the type of $CCl_2=CH-CH_2X$ and $HCCl_2CH=CH-X$ (X = −COOH, −CN) do not isomerize under the action of acids.

4. It was established that the acid obtained by Auwers and Wissebach by reduction of γ,γ,γ-trichlorocrotonic acid with zinc and acetic acid in ethyl alcohol is not γ,γ-dichlorocrotonic acid, as assumed by the authors, but γ,γ-dichlorovinylacetic acid.

5. It was shown that the two-step reduction by Auwers and Wissebach of γ,γ,γ-trichlorocrotonic acid to crotonic acid proceeds with a double isomerization which was not detected by these authors. Consequently the reduction of γ,γ,γ-trichlorocrotonic acid to crotonic acid, which was performed by Auwers and Wissebach, cannot serve to establish the configuration of crotonic acid.

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DERIVATIVES OF UNSATURATED PHOSPHINIC ACIDS

I. SYNTHESIS OF CHLORIDES OF β-ALKOXY (PHENOXY) - VINYL - PHOSPHINIC ACIDS

K. N. Anisimov and A. N. Nesmeyanov

The addition of salts of mercury to vinylethers (and esters), studied by one of us and Lutsenko [1], proceeds in such a manner that the mercury is attached to the olefinic carbon linkage, while the alkyl radical of the vinyl ether links with oxygen and acquires a carbonyl function

$$ROCH{=}CH_2 + HgAC_2 \rightarrow AcHg{-}CH_2{-}CHO.$$

In the present paper we investigate the addition of phosphorus pentachloride to alkyl (aryl) vinyl ethers and study the properties of the resultant addition products. The reaction of addition of phosphorus pentachloride to unsaturated compounds was discovered by March and Gardner [2] who showed that camphene reacts with phosphorus pentachloride to give an addition product forming, after treatment with water, camphenephosphinic acid.

Harnist [3] added phosphorus pentachloride to styrene, diphenylethylene, isobutene and ethynylbenzene. Bulle [4] carried out the reaction of phosphorus pentachloride with indene. Bergman and Bondi [5] made a fairly detailed study of the addition of phosphorus pentachloride to a series of unsaturated aromatic compounds; they established that addition of phosphorus pentachloride readily takes place, mainly to unsymmetrically phenylated ethylenes.

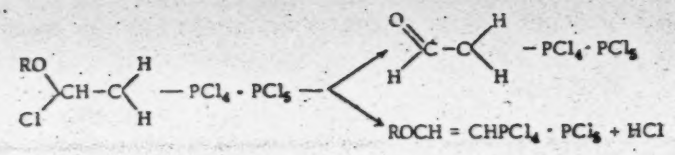
The same line of investigation was followed by Kosolapoff [6] and Bachmann [7] who showed that addition of phosphorus pentachloride to the double bond proceeds in such a way that the PCl_4 group adds on to the most hydrogenated carbon atom while an atom of chlorine adds on to the least hydrogenated carbon. The products of addition are isolated in the form of double compounds with phosphorus pentachloride.

The addition of phosphorus pentachloride to vinyl ethers has not hitherto been investigated. It was established that gradual addition of vinyl ethers to a suspension of phosphorus pentachloride in benzene leads to a very violent reaction with formation of a solid, crystalline product of addition from which gaseous hydrogen chloride begins to come off more intensively the higher the temperature of the reaction mass. Addition of phosphorus pentachloride to vinyl ethers follows the Markovnikov rule. In this manner we obtained products of addition of phosphorus pentachloride to methyl vinyl, ethyl vinyl, n-propyl vinyl, isopropyl vinyl, n-butyl vinyl, isobutyl vinyl, isoamyl vinyl, n-hexyl vinyl and phenyl vinyl ethers. The addition compounds are crystalline substances which lose hydrogen chloride at room temperature and are extremely easily hydrolyzed in the air. These properties prevented us from isolating the compounds in the pure state. Subsequently the addition products were worked up with sulfur dioxide (Michaelis [8]) until completely transformed into liquid. After the solvent, the phosphorus oxychloride and the thionyl chloride had been driven off, the residue was kept in the vacuum of a water jet pump on a boiling water bath until the whole of the hydrogen chloride was split off; it was fractionated in vacuum to give the chlorides of the β-alkoxy (phenoxy)-vinylphosphinic acids. The reactions are expressed by the following equations:

$$ROCH{=}CH_2 + 2PCl_5 = ROCHCl{-}CH_2PCl_4 \cdot PCl_5;$$

$$ROCHCl{-}CH_2PCl_4 \cdot PCl_5 + 2SO_2 = ROCH{=}CHPOCl_2 + POCl_3 + 2SOCl_2 + HCl\,.$$

Thus the addition of phosphorus pentachloride to vinyl ethers proceeds just like the addition to other compounds with an olefinic bond and quite differently to the addition of mercury salts. The dimeric molecule, P_2Cl_{10}, adds on; the alkyl radical of the alkoxyl remains intact and hydrogen chloride is split off with regeneration of the unsaturated structure of the vinyl ether. After the addition of phosphorus pentachloride the hydrogen atoms of the methylene linkage are found to be extremely mobile and of the two possible parallel reactions only one is realized, namely, the one involving cleavage of this hydrogen as HCl



We made use of this reaction for the synthesis of a large number of diverse functional derivatives of alkoxyvinylphosphinic acids.

EXPERIMENTAL

Vinyl ethers were prepared by the method of Favorsky and Shostakovsky [9]. Chlorides of β-alkoxyvinylphosphinic acids were synthesized in the following manner. Experiments were carried out in a dry flask protected against atmospheric moisture by a calcium chloride tube. To a weighed amount of 0.4 mole phosphorus pentachloride in 150 ml dry benzene was gradually added from a dropping funnel, with shaking and water cooling, 0.2 mole alkyl vinyl ether. Considerable heat was developed and a dense crystalline precipitate was formed; a short time after the whole of the ether had been run in, the precipitate started to give off hydrogen chloride. The following day sulfur dioxide was passed into the product at room temperature until the crystalline precipitate was completely transformed into a liquid. The reaction proceeded with heat development; cooling was sometimes employed. The product was transferred to a Claisen flask and the benzene, $POCl_3$ and $SOCl_2$ were distilled off in vacuum; the mixture was kept in the vacuum of a water jet pump on a hot water bath until the whole of the HCl had split off and the residue was then fractionated in vacuum. This method was used for the synthesis of the chlorides of the β-alkoxy (phenoxy)-vinyl phosphinic acids whose properties are set forth in the table.

β-Methoxyvinylphosphinyl chloride $CH_3OCH = CHPOCl_2$. Into the previously prepared addition product ($CH_3OCHCl-CH_2PCl_4PCl_3$) was passed SO_2 until transformation of the crystalline mass into a liquid. After the solvent, the $POCl_3$ and $SOCl_2$ had been driven off, the residue was fractionated in vacuum. β-Methoxyvinylphosphinyl chloride has b.p. 76° (1.5 mm); n_D^{20} 1.5052; d_4^{20} 1.4186.

	Found %	P 17.38; 17.33;	C 20.17; 20.49;	H 2.62; 2.62;	Cl 40.65; 40.18
$C_3H_5O_2Cl_2P$.	Calculated %	P 17.71	C 20.57;	H 2.85;	Cl 40.57

TABLE

Formula	B.p. in °C (p in mm. mercury column)		n_D^{20}	d_4^{20}	Yield in %
$CH_3-O-CH = CHPOCl_2$	76	(1.5)	1.5052	1.4186	11
$C_2H_5-O-CH = CHPOCl_2$	84	(2)	1.4969	1.3221	87
$n-C_3H_7-O-CH = CHPOCl_2$	101	(3)	1.4945	1.2823	78
$i-C_3H_7-O-CH = CHPOCl_2$	m.p. 52–53				76
$n-C_4H_9-O-CH = CHPOCl_2$	107.5	(2)	1.4926	1.2384	81
$i-C_4H_9-O-CH = CHPOCl_2$	96	(1)	1.4900	1.2318	78
$(CH_3)_2CH-(CH_2)_2O-CH=CHPOCl_2$	112	(1)	1.4876	1.2058	95
$n-C_6H_{13}O-CH = CHPOCl_2$	126	(2)	1.4890	1.2083	92
$C_6H_5-O-CH = CHPOCl_2$	131	(2)	1.5708	1.3710	75

β-Ethoxyvinylphosphinyl chloride $C_2H_5OCH = CHPOCl_2$. SO_2 was passed into the product of addition ($C_2H_5-OCHCl-CH_2PCl_4 \cdot PCl_3$) until the substance had turned liquid the solvent, $POCl_3$ and $SOCl_2$ were then distilled off at the ordinary pressure and the residue at 2 mm. Yield 33 g (87% of theory) with b.p. 84.5–85° (2 mm); n_D^{20} 1.4969; d_4^{20} 2 3321.

	Found %	P 16.19; 16.47;	C 37.18; 37.45
$C_4H_7O_2Cl_2P$.	Calculated %	P 16.40;	C 37.56

β- n-Propoxyvinylphosphinyl chloride $n-C_3H_7OCH = CHPOCl_2$. The chloride was synthesized in the above-described conditions. Yield 32 g (78% of theory) with b.p. 101° (3 mm); n_D^{20} 1.4925; d_4^{20} 1.2823.

	Found %	P 15.44 15.26;	C 29.98; 30.21;	H 3.95; 3.90;	Cl 34.81; 34.92
$C_5H_9O_2Cl_2P$.	Calculated %	P 15.27	C 29.55;	H 4.43	Cl 34.97

β-Isopropoxyvinylphosphinyl chloride i-$C_3H_7OCH = CHPOCl_2$. Synthesis conditions as above. Yield 31 g chloride (76% of theory) with b.p. 92° (3 mm); m.p. 52-53°.

	Found %:	P 15.37; 15.00;	C 29.73; 29.40;	H 4.28; 4.46;	Cl 34.94; 34.91
$C_5H_9O_2Cl_2P$.	Calculated %:	P 15.27;	C 29.55;	H 4.43;	Cl 34.97

β-n-Butoxyvinylphosphinyl chloride n-$C_4H_9OCH = CHPOCl_2$. The synthesis was effected in the above-described conditions. Yield 35.5 g (81% of theory) with b.p. 107.5° (2 mm); n_D^{23} 1.4926; d_4^{23} 1.2384.

	Found %:	P 14.14; 14.27;	Cl 32.60; 32.80
$C_6H_{11}O_2Cl_2P$.	Calculated %:	P 14.28	Cl 32.71

Isobutoxyvinylphosphinyl chloride i-$C_4H_9OCH = CHPOCl_2$. Preparation by the above-described method. Yield 34 g (78% of theory) with b.p. 96° (1 mm); n_D^{23} 1.4900; d_4^{23} 1.2318.

	Found %:	P 14.43; 14.24;	C 33.26; 33.36;	H 4.95; 5.10;	Cl 32.56; 32.78
$C_6H_{11}O_2Cl_2P$.	Calculated %:	P 14.28;	C 33.17;	H 5.06;	Cl 32.71

β-Isoamyloxyvinylphosphinyl chloride $(CH_3)_2CH-CH_2-CH_2OCH = CHPOCl_2$. Same conditions for preparation. 44 g was synthesized (95% of theory) with b.p. 112° (1 mm); n_D^{20} 1.4876; d_4^{20} 1.2058.

	Found %:	C 36.19; 36.42;	H 5.62; 5.30;	P 13.23; 13.20
$C_7H_{13}O_2Cl_2P$.	Calculated %:	C 36.36;	H 5.62;	P 13.41

β-n-Hexyloxyvinylphosphinyl chloride n-$C_6H_{13}OCH = CHPOCl_2$. This compound was obtained in a yield of 45 g (92% of theory) with b.p. 126° (2 mm); n_D^{23} 1.4890; d_4^{23} 1.2083.

	Found %:	P 12.63; 12.69;	Cl 28.94; 28.82
$C_8H_{15}O_2Cl_2P$.	Calculated %:	P 12.65;	Cl 28.97

β-Phenoxyvinylphosphinyl chloride $C_6H_5OCH = CHPOCl_2$ was synthesized by the same method as for the chlorides of β-alkoxyvinylphosphinic acids; yield 75% of theory; b.p. 131° (2 mm); n_D^{23} 1.5708; d_4^{23} 1.3710.

	Found %:	P 12.84; 12.89;	C 40.75; 40.90;	H 2.79; 2.97	
$C_8H_7O_2Cl_2P$.	Calculated %:	P 13.08;	C 40.50;	2.95	

Chlorides of β-alkoxy (phenoxy)vinylphosphinic acids are also obtained in good yield by acting on the addition products ($ROCHCl-CH_2PCl_4 \cdot PCl_5$) with carboxylic acids and also with water. The chlorides of β-alkoxy(phenoxy)-vinylphosphinic acids that we studied were transparent liquids (except the solid i-$C_3H_7OCH = CHPOCl_2$), distilling in vacuum without decomposition, possessing a weak acid chloride odor and stable on keeping. All the chlorides are soluble in common organic solvents, are slowly hydrolyzed by cold water and more quickly by hot; they all decolorize bromine water.

SUMMARY

1. The addition of phosphorus pentachloride to vinyl ethers was studied.

2. A simple and convenient method was developed for synthesis of the dichlorides of β-alkoxy(phenoxy)vinylphosphinic acids.

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DIPOLE MOMENTS OF ESTERS OF ORTHOPROPIONIC AND ORTHOFORMIC ACIDS

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In previous communications we gave the dipole moments of orthocarbonic, orthosilicic and orthotitanic acids and discussed their possible structure [1]. On the basis of calculation of the dipole moments of various models of esters of orthocarbonic, orthosilicic and orthotitanic acids and of calculation of the interatomic distances of these models (allowing for the radius of action of van der Waal forces for methyl groups), we showed that the change in arrangement of the alkoxy groups of esters of orthocarbonic, orthosilicic and orthotitanic acids and the possibility of free rotation or restricted oscillation may be governed by a difference in the covalent radii of the central atom.

Continuing our studies of the dipole moments of esters of ortho acids, it appeared of interest to measure the dipole moments of esters of orthopropionic and orthoformic acids. Measurements were made of the moments of the esters set forth in Table 1.

TABLE 1

Formula of compound	Dipole moment in D
$CH_3CH_2C(OC_2H_5)_3$	1.93
$CH_3CH_2C(OC_3H_7)_3$-n	1.92
$CH_3CH_2C(OC_4H_9)_3$-n	1.84
$CH_3CH_2C(OC_6H_{13})_3$	1.90
$CH_3CH_2C)OC_8H_{17})_3$	2.00
$HC(OCH_3)_3$	1.88
$HC(OC_2H_5)_3$	1.90
$HC(OC_3H_7)_3$-n	1.92

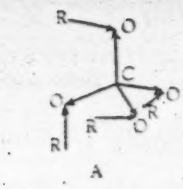
Measurements of the moments of esters of orthopropionic acid gave values of 1.84 to 2.00 D and a mean value of 1.92 D. The mean value for the dipole moments of esters of orthoformic acid was 1.90 D. As we see, the dipole moments of esters of orthopropionic and orthoformic acids are considerably higher than those of esters of orthocarbonic acid (1.1 D).

Esters of orthopropionic and orthoformic acid possess a tetrahedral structure of the central grouping. In the distribution of the dipole moments of the individual bonds, the esters of orthopropionic acid are similar to esters of phosphorous acid since the dipole moment of the C−C bond is assumed to be zero; the distribution of the dipole moments of the individual bonds in esters of orthoformic acid is similar to the distribution of the dipole moments of the individual bonds in esters of phosphorous acid since the dipole moment of the C−H bond is assumed to be 0.4 D. Esters of orthopropionic and orthoformic acids contain three irregular alkoxy groups which make an angle of 110° with the direction of the C−O bond.

In calculating the dipole moments of molecular models of esters of orthopropionic and orthoformic acids, we assumed the dipole moment of the R → O bond to be 1.12 D, that of the C → O bond 0.9 D, and that of the H → C bond 0.4 D [2]. The valence angle of oxygen is 110°; that of the carbon 109° 30'. The dipole moment of the molecule of orthopropionic esters, calculated on the assumption of completely free rotation of the three OR groups around the C−O bonds, is 1.96 D and is almost identical with the experimentally determined value (1.92 D).

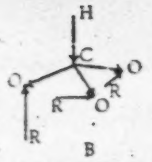
Calculation of the interatomic distances of molecular models, making allowance for the covalent radius of carbon and the radius of the fields of action of the van der Waals forces for the methyl group (2.0 A), shows that completely free rotation of the OR groups round the C−O bonds is impossible in esters of orthopropionic acid due to the considerable influence of the fields of action of van der Waals forces in all positions taken up during free rotation of the OR groups round the C−O bonds. The interatomic distance of C−O is 1.43 A.

We studied the dipole moments and interatomic distances of all possible models with synchronous movement of three OR groups together, and of the fourth OR group rotating independently, also of models with pairwise disposition of two OR groups in one plane and of a third OR group and the $C-CH_2-CH_3$ in another plane perpendicular to the first. However, among all these models we failed to find one whose dipole moment approximated to the experimentally found value; nor could we find one which reproduced the van der Waals fields of force of the methyl and methylene groups. The smallest area of superposition of the van der Waals fields of force of the methyl and methylene groups is exhibited by the rigid model A (Fig. 1), but its dipole moment is 1.15 D and very different from the experimental value.



A

Fig. 1



B

Fig. 2

Esters of orthoformic acid have a dipole moment with a mean value of the order of 1.90 D. The dipole moment of the molecule of an ester of orthoformic acid with tetrahedral distribution of three C–O bonds and one C–H bond and free rotation of the three R–O groups round the C–O bonds proved to be 1.86 D and barely different from the experimental magnitude (1.90 D). Esters of orthoformic acid differ from esters of orthopropionic acid in that the former contain a C–H bond in place of a hydrocarbon chain. The radius of action of the van der Waals forces for the hydrogen atom is taken to be 1.2 A [3].

We have studied the dipole moments and interatomic distances of molecular models developed on rotation of the OR groups around the C–O bonds and we found that the free rotation of OR groups around the C–O bonds in esters of orthoformic acid is also impossible due to the considerable influence of the van der Waals fields of force of the methyl and methylene groups and of the field of action of the van der Waals forces of the hydrogen atom.

Consideration of the dipole moments and interatomic distances of rigid models of esters of orthoformic acid, when three OR groups are rotating synchronously round the C–O bonds, shows that none of these models can be accepted for the esters of orthoformic acid since they are all greatly influenced by the fields of action of the van der Waals forces of the methyl group and the hydrogen atom. A study of the dipole moments and interatomic distances of models with synchronization of movement of two OR groups in one plane and with a third OR group in the plane of the C–H bond shows that model B (Fig. 2) has the least area of superposition of the spheres of action of the van der Waals forces of the methyl groups and the hydrogen atom. However, the dipole moment of this model is 1.16 D, 0.74 D less than the experimentally found magnitude.

Consequently, nowithstanding that the mean magnitude of the dipole moment for esters of orthopropionic and orthoformic acids nearly exactly corresponds to the dipole moment of a molecule in which allowance is made for free rotation of three OR groups round the C–O bonds, on the basis of a study of the interatomic distances of models of esters we arrive at the conclusion that rotation of the OR groups round the C–O bonds is impossible in esters of orthopropionic and orthoformic acids.

A study of models with synchronization of the movement of three alkoxy groups or paired synchronized movement of the alkoxy groups in two directions perpendicular to each other likewise did not enable us to clarify the character of the possible oscillations of the OR groups in esters of orthopropionic and orthoformic acids if we assume a radius of action of 2.0 A for the van der Waals fields of force of the methyl and methylene groups and a radius of 1.2 A for the field of force of the hydrogen atom. It is most probable that the OR groups and the CH_3CH_2C chain in esters of orthopropionic acid are arranged pairwise in two planes perpendiculat to each other (model A, Fig. 1); for esters of orthoformic acid the most probable are model B (Fig. 2) and a model in which three OR groups are arranged in a plane perpendicular to the plane of the C–H bond. A model with pairwise disposition of the lakoxy groups in two planes perpendicular to each other has been proposed for esters of orthopropionic acid by one of us and Yuldasheva on the basis of measurements of the parachors of esters of orthopropionic acid [4].

Recently we measured the dipole moments of $Sb(OC_2H_5)_5$, $W(OC_6H_5)_6$ and $W(OC_6H_4CH_2)_6$. The dipole moments of these compounds were found to be 2.29, 2.13 and 2.07 D respectively. These compounds contain 5 and 6 irregular OC_2H_5, OC_6H_5 and $OC_6H_4CH_2$ groups and have a symmetrical structure. Their probable structure is a model of a bipyramid with an equilateral triangle for $Sb(OC_2H_5)_5$ and a rectangle for $W(OC_6H_5)_6$ and $W(OC_6H_4CH_3)_6$ at the base. Considering the possible models for these compounds, it can be stated that the model of the bipyramid leads to mutual compensation of the dipole moments of the Sb–O and W–O bonds, and the dipole moments of these compounds is governed only by the disposition and number of irregular groups. This condition permitted us to calculate the dipole moments of the rigid structures and of the model with free rotation of the irregular groups for these esters since the dipole moments of the Sb–O and W–O bonds are unknown.

The dipole moment of the model of the trigonal bipyramid of $Sb(OC_2H_5)_5$, for the condition of perfectly free rotation of the ethoxy groups round the respective Sb–O bonds, was calculated from the formula of Svirbely and Lander [5] and is equal to 2.19 D, which is close to the experimental value of 2.29 D. The dipole moment of the model of the tetragonal bipyramid of $W(OC_6H_5)_6$, for the condition of completely free rotation of the six irregular phenoxy groups round the respective W–O bonds, was found by the formula of Svirbely and Lander [5] to be 2.45 D, or 0.32 D more than the experimental value of 2.13 D. The dipole moment of the model of $W(OC_6H_4CH_3)_6$, for the condition of fully free rotation of the six $OC_6H_4CH_3$ groups round the W–O bonds, is 2.93 D or 0.8 D higher than the experimental value.

We made the following assumptions in our calculations of the dipole moments of the molecular models: dipole moment of the $O-C_2H_5$ bond 1.12 D; that of the $O-C_6H_5$ bond 1.0 D; that of the $O-C_6H_4CH_3$ bond 1.20 D; the corresponding data were calculated from the dipole moment of diphenyl ether, equal to 1.14 D, and the dipole moment of $(C_6H_4CH_3)_2O$ equal to 1.38 D [6]. The O–C–O angle is 110°. However, the calculated interatomic distances of the models possible with free rotation of the irregular groups, allowing for the covalent radius of antimony (1.40 A) and the covalent radius of tungsten (1.39 A) and the effective thickness of the aromatic molecule of 3.7 A [3], shows that completely free rotation of the irregular groups in the compounds $Sb(OC_2H_5)_5$ and $W(OC_6H_5)_6$ is impossible due to steric hindrance between the ethoxyl groups and the aromatic rings.

The least influence of the effective thickness of the aromatic ring and of the spheres of action of the van der Waals forces is attained when the aromatic ring is arranged in the plane of the rectangular base of the tetragonal bipyramide while the ethoxy group is arranged in the plane of the triangular base of the trigonal bipyramid. The dipole moment of $Sb(OC_2H_5)_5$ is then governed only by the disposition of the two dipole moments of the $-OC_2H_5$ bonds, since the dipole moments of the three $O-C_2H_5$ bonds in the plane of the triangular base of the bipyramid are mutually compensated and are equal to zero if the dipole moments of these groups are directed to different sides, or equal to 2.10 D if the dipole moments of two $O-C_2H_5$ bonds are directed to the same side.

In the molecules of $W(OC_6H_5)_6$ and $W(OC_6H_4CH_3)_6$ the dipole moments of four irregular groups, distributed in the plane of the rectangular base of the bipyramid, are also mutually compensated and the resultant dipole moment of $W(OC_6H_5)_6$ and $W(OC_6H_4CH_3)_6$ is equal to zero if the dipole moments of the $O-C_6H_5$ and $O-C_6H_4CH_3$ bonds are oppositely directed, or equal to 1.88 and 2.26 D respectively if the dipole moments of these bonds are directed to one side. The dipole moment of $Sb(O\cdot C_2H_5)_5$ allowing for the free rotation of two $O-C_2H_5$ groups, is 1.50 D; for $W(OC_6H_5)_6$ it is 1.33 D; for $W(O\cdot C_6H_4CH_3)_6$ it is 1.59 D.

The dipole moment of the model with the greatest superposition of the spheres of action of the van der Waals forces is 2.88 D for $Sb(OC_2H_5)_5$ and 3.76 D for $W(OC_6H_5)_6$.

Consequently the experimentally found dipole moments of $Sb(OC_2H_5)_5$ (2.29 D), of $W(OC_6H_5)_6$ (2.13 D) and of $W(OC_6H_4CH_3)_6$ (2.10 D) do not correspond either to the maximum or the minimum value of the dipole moments calculated for the various models. The dipole moments of molecules least affected by the spheres of action of the van der Waals forces [$Sb(OC_2H_5)_5$ 1.50 D; $W(OC_6H_5)_6$ 1.33 D, and $W(OC_6H_4CH_3)_6$ 1.59 D] differ considerably from the respective experimental values of 2.29, 2.13, and 2.10 D.

EXPERIMENTAL

The dielectric constants and densities of benzene solutions of esters of orthopropionic and orthoformic acids were determined at 25°. Dipole moments were calculated from the formula:

$$\mu = 0.0127 \cdot 10^{-18} \sqrt{(P_\infty - P_{el} - P_{at}) \cdot 298},$$

where $MR = P_{el}$; $P_{at} = 5\% P_{el}$.

We prepared the esters of orthopropionic acid by the transesterification of ethyl orthopropionate [4] with the appropriate alcohol in presence of conc. phosphoric acid. They had the following constants (Table 2).

TABLE 2

Formula of compound	B.p. in °C (p in mm mercury column)	n_D^{25}	d_4^{25}	MR	
				calculated	found
$CH_3CH_2C(OC_2H_5)_3$	60 (17)	1.3987	0.8826	48.69	48.30
$CH_3CH_2C(OC_3H_7)$-n	92.5–93 (14)	1.4100	0.8831	62.54	61.24
$CH_3CH_2C(OC_4H_9)_3$-n	117–117.5 (5 mm)	1.4208	0.8699	76.40	75.80
$CH_3CH_2C(OC_6H_{13})_3$	172–173.5 (4)	1.4329	0.8668	104.1	103.4
$CH_3CH_2C(OC_8H_{17})_3$	215–218 (3)	1.4404	0.8635	131.8	131.0

The methyl ester of orthoformic acid was synthesized by reaction of sodium methoxide with chloroform in ethereal solution. The ethyl ester of orthoformic acid was obtained by reacting sodium ethoxide with chloroform, while cooling, in alcoholic solution [7]. The butyl ester of orthoformic acid was obtained by transesterification of the ethyl ester with n-butyl alcohol in presence of phosphoric acid. The orthofumaric esters had the constants set forth in Table 3.

Antimony pentaethoxide with b.p. 160–162° (4.5 mm) was prepared by interaction of sodium ethoxide and antimony pentachloride in benzene [8].

TABLE 3

Formula of compound	B.p. in °C (p in mm mercury column)	d_4^{25}	n_D^{25}	MR	
				calculated	found
$(CH_3O)_3CH$	99–99.5	0.9645	1.3795	26.60	26.45
$(C_2H_5O)_3CH$	145–146	0.8870	1.3909	39.44	39.69
$(C_4H_9O)_3CH$-n	112–113 (6)	0.8726	1.4187	67.16	67.17

Tungsten hexaphenoxide [9] with m.p. 98° was prepared by interaction of tungsten hexachloride with 10 parts by weight of phenol. The precipitate was washed with alcohol and recrystallized from alcohol. Dark-red needles and leaflets melting at 98°.

WO_3. Calculated 0.02319 g
WO_3. Found 0.02320 g

Hexa(p-Tolyloxy) tungsten with m.p. 134-135° was prepared by reaction of 25 g p-cresol with 3 g tungsten hexachloride. Hydrogen chloride started to come off in the cold. The reaction mixture was heated to the boil for 10-15 min. and gave a dark, cherry-red solution. Addition of a small quantity of absolute alcohol followed by standing overnight at 0° resulted in deposition of black crystals which were drained, washed on the filter with absolute alcohol, yield 2.7 g. After recrystallization from absolute alcohol in a Soxhlet apparatus, black crystals with m.p. 130-131° were obtained. The black residue on the filter was extracted with boiling benzene; to the benzene solution was added an equal volume of alcohol. After a short time, black crystals came down. Recrystallization from a large quantity of benzene gave needles with a dark garnet color, m.p. 134-135°.

WO_3. Calculated 0.008864 g
WO_3. Found 0.0088 g

The dielectric constants, densities and polarizations of benzene solutions of various concentrations of the compounds at 25° are set forth in Tables 4 to 14.

TABLE 4

$CH_3CH_2C(OC_2H_5)_3$

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.006011	2.2861	0.8730	27.00	116.4
0.003364	2.2833	0.8725	26.93	123.3
0.007904	2.2970	0.8725	27.28	113.0
0.008967	2.2982	0.8725	27.35	108.5
0.010820	2.3029	0.8725	27.48	107.1
0.013280	2.3096	0.8725	27.66	106.1

$P_\infty = 128.0$; $P_{A+E} = 50.7$
$P_{or} = 77.3$; $\mu = 1.93D$

TABLE 5

$CH_3CH_2C(OC_3H_7)_3$-n

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.004453	2.2913	0.8742	27.10	138.2
0.006032	2.2974	0.8742	27.26	136.2
0.007147	2.3008	0.8742	27.26	134.9
0.010150	2.3101	0.8742	27.64	130.9
0.011660	2.3166	0.8742	27.84	131.3
0.010910	2.3130	0.8742	27.73	130.4

$P_\infty = 141.0$; $P_{A+E} = 64.30$
$P_{or} = 76.70$; $\mu = 1.92D$

TABLE 6

$CH_3CH_2C(OC_4H_9)_3$-n

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.001843	2.2789	0.8740	26.80	142.1
0.002102	2.2790	0.8740	26.85	141.9
0.005449	2.2852	0.8740	27.16	125.7
0.003961	2.2831	0.8740	27.02	132.4
0.006794	2.2902	0.8740	27.29	129.5
0.004172	2.2847	0.8740	27.05	137.0

$P_\infty = 150.0$; $P_{A+E} = 79.5$;
$P_{or} = 70.5$; $\mu = 1.84$ D

TABLE 7

$CH_3CH_2C(OC_6H_{13})_3$

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.002816	2.2850	0.8746	27.04	183.2
0.004553	2.2885	0.8746	27.18	170.5
0.005591	2.2918	0.8746	27.41	169.5
0.006276	2.2931	0.8746	27.48	166.3
0.007104	2.2943	0.8746	27.57	162.6
0.007975	2.2975	0.8746	27.70	163;4

$P_\infty = 184.0$; $P_{A+E} = 108.6$;
$P_{or} = 75.4$; $\mu = 1.90$ D

TABLE 8

$CH_3CH_2C(OC_8H_{17})_3$

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.002116	2.2804	0.8734	27.02	215.6
0.002602	2.2821	0.8736	27.09	213.0
0.003980	2.2865	0.8734	27.34	209.9
0.003131	2.2830	0.8734	27.34	207.3
0.005117	2.2880	0.8734	27.48	198.9
0.005856	2.2904	0.8734	27.59	197.0

P_∞ = 221.0; P_{A+E} = 137.6;
P_{or} = 83.4; μ = 2.00 D

TABLE 9

$HC(OCH_3)_3$

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.004101	2.2887	0.8735	26.91	98.04
0.008074	2.3014	0.8742	27.11	87.38
0.012610	2.3120	0.8749	27.29	79.58
0.015600	2.3324	0.8751	27.62	89.77
0.026360	2.3665	0.8768	28.87	85.36
0.021400	2.3521	0.8764	27.90	86.45

P_∞ = 100.0; P_{A+E} = 26.72;
P_{or} = 73.28; μ = 1.88 D

TABLE 10

$HC(OC_2H_5)_3$

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.002999	2.2848	0.8730	26.92	120.2
0.005883	2.2962	0.8730	27.14	114.1
0.008883	2.3088	0.8730	27.39	114.4
0.012150	2.3211	0.8730	27.65	110.4
0.01520	2.3330	0.8730	27.91	111.0
0.01753	2.3415	0.8730	28.08	110.0

P_∞ = 117.0; P_{A+E} = 41.67;
P_{or} = 75.33; μ = 1.90 D

TABLE 11

$HC(OC_4H_9)_3$

C_2	ϵ_{12}	d_{12}	P_{12}	P_2
0.002468	2.2840	0.8728	26.96	149.0
0.004551	2.2924	0.8728	27.19	137.6
0.006772	2.3022	0.8728	27.45	142.9
0.008849	2.3114	0.8728	27.69	143.6
0.012040	2.3232	0.8728	28.04	141.5
0.010660	2.3185	0.8728	27.88	141.3

P_∞ = 147.00; P_{A+E} = 70.53
P_{or} = 76.47; μ = 1.92 D

TABLE 12

$Sb(OC_2H_5)_5$

C_2	ϵ_{12}	d_{12}	n_D^{20}	MR_{12}	MR_2	P_{12}	P_2
0.002558	2.2929	0.8783	1.4959	26.20	70.22	27.02	189.9
0.003238	2.2960	0.8793	1.4960	26.25	71.09	27.11	181.0
0.004887	2.3058	0.8819	1.4960	26.32	71.00	27.31	170.3
0.003566	2.3091	0.8805	1.4959	26.25	65.85	27.29	217.2
0.005983	2.3162	0.8838	1.4959	26.35	69.40	27.50	177.7
0.007346	2.3302	0.0059	1.4958	26.43	69.19	27.72	176.9

P_∞ = 185.0; P_{A+E} = 75.60; P_{or} = 109.4; μ = 2.29 D; P_{el} = 72.0

TABLE 13

$W(OC_6H_5)_6$

C_2	ϵ_{12}	d_{12}	n_D^{20}	MR_{12}	MR_2	P_{12}	P_2
0.00048	2.2754	0.8755	1.4961	26.18	191.0	26.75	278.5
0.00087	2.2799	0.8767	1.4976	26.29	254.4	26.84	305.9
0.00135	2.2817	0.8784	1.4985	26.34	247.7	26.92	272.1
0.001530	2.2840	0.8798	1.4991	26.44	234.4	26.99	260.9
0.00061	2.2765	0.8774	1.4968	26.19	194.1	26.73	235.4

P_∞ = 283.00; P_{A+E} = 189.00; P_{or} = 94.00; μ = 2.13 D; P_{el} = 180.0

TABLE 14

$W(OC_6H_4CH_3)_6$

C_2	ϵ_{12}	d_{12}	n_D^{20}	MR_{12}	MR_2	P_{12}	P_2
0.00033	2.2738	0.8755	1.4953	26.12	98.79	26.67	254.8
0.00071	2.2788	0.8768	1.4968	26.24	234.1	26.64	317.0
0.00090	2.2797	0.8774	1.4967	26.26	212.5	26.87	303.3
0.001116	2.2819	0.8784	1.4977	26.34	242.0	26.92	301.6
0.001322	2.2842	0.8786	1.4984	26.40	262.5	26.98	315.6
0.0005	2.2769	0.8746	1.4963	26.22	300.5	26.79	397.7

$P_\infty = 310.0$; $P_{A+E} = 218.4$; $P_{or} = 91.6$; $\mu = 2.10$ D; $P_{el} = 208.0$

SUMMARY

1. Measurements were made of the dipole moments of ethyl, n-propyl, n-butyl, hexyl and octyl esters of orthopropionic acid (mean value of dipole moment 1.92 D), and of the methyl, ethyl and n-butyl esters of orthoformic acid (mean value 1.90 D).

2. Measurements were made of the dipole moments and refractivities of antimony pentaethoxide (2.29 D), tungsten hexaphenoxide (2.13 D) and hexa-p-tolyloxytungsten (2.10 D).

3. Calculation of the interatomic distances of various molecular models, allowing for the radius of the spheres of action of the van der Waals forces of the methyl and methylene groups (2.0 A) and the radius of the spheres of action of the van der Waals forces of the hydrogen atom (1.2 A), shows that free rotation of the irregular groups is impossible in these compounds.

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PARACHORS OF MONOESTERS OF ETHYLPHOSPHONOUS ACID

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As was shown in previous communications, the structural peculiarities of certain types of organic molecules, characterized by the presence of a certain spatial distribution of long hydrocarbon chains, can be readily detected from the magnitudes of the parachors. On calculating the theoretical values of the parachors by the method of "group values", these peculiarities of structure are manifested in corrections for bending and parallelity of the chains and the value of the molecular parachor is reduced.

A current problem of great interes which has not been adequately clarified is that of the nature and causes of appearance of corrections for parallelity. Up to now we have studied the parachors of compounds in which the fall of molecular parachor was brought about by interaction between the carbon atoms of two or three chains inside one molecule and by the corresponding distribution of the chains parallel to one another.

Interesting examples, in which the possibility of intramolecular reaction of chains is excluded, are the monoesters of ethylphosphonous acid. The monoesters of ethylphosphonous acid are analogs of dialkylphosphorous acids in which one hydrocarbon chain is directly attached to phosphorus. Study of their parachors is therefore of interest because of the possibility of establishing whether or not they associate. Association occurs in certain dialkylphosphorous and phosphonous acids [1].

In this communication we present our data for the parachors of a series of monoesters of ethylphosphonous acid, synthesized by Rizpolozhensky [2]; their constants are set forth in Table 1.

TABLE 1

Formula	B.p. in °C (p in mm mercury column)		d_4^{20}	n_D^{20}	γ^{20}
CH_3	65–66	(11)	1.0795	1.4273	34.5
C_2H_5	68–69	(9)	1.0195	1.4242	30.8
n-C_3H_7	80	(9)	0.9866	1.4285	28.8
i-C_3H_7	69.5–70	(10)	0.9820	1.4233	27.7
n-C_4H_9	68	(1.5)	0.9753	1.4340	29.5
i-C_4H_9	86.5–87	(8)	0.9688	1.4300	28.1
C_6H_{13}	87.5–88	(1.5)	0.9507	1.4374	29.4
C_7H_{15}	102	(3.5)	0.9383	1.4395	29.1
C_8H_{17}	102.5–103	(1)	0.9316	1.4440	29.1
C_9H_{19}	122–123	(3.5)	0.9216	1.4430	29.4

In Table 2 are set forth the theoretical values of the parachors calculated for the monomeric form of the monoesters of ethylphosphonous acid with allowance for the β-correction for the bending of the ester chain (1.4 unit) ([P] calc. I). The group value of $C_2H_5P\begin{matrix}O(C)\\ \diagdown\\ \diagup\\ OH\end{matrix}$ = 187.0 units was calculated by the usual method from the parachor of the methyl ester (a correction for the β-carbon of the ethyl chain of −2.0 units [3] enters into the group value).

As we see from Table 2, the experimental parachors have lower values than the theoretical values $[P]_{calc.I}$. The obtained deviations, which exceed the experimental error, cannot be accounted for by inadequate purity of the investigated compounds. Repeated syntheses and purification did not appreciably change the values of the parachors. Evidently in this case the low values of the parachors must be explained by the presence of structural factors which were not allowed for in the corrections introduced. Low parachor values were obtained for esters of fumaric acid [4] in which we can hardly suggest that possibility of parallel arrangement of chains in view of the trans-position of the carboxyl groups; the same phenomenon has been observed with esters of terephthalic acid [5]

and a number of other acids in which intramolecular interaction of chains is likewise highly improbable.

The compared values of calculated and found parachors for esters of fumaric and terephthalic acids were obtained on the assumption of a structure with parallel chains of different molecules and therefore with introduction of a correction in the value of the molecular parachor of −1.1 unit (1/2 ‖) per carbon atom of the ester chain at the β-carbon.

The parachors of monoesters of ethylphosphonous acid, calculated with a correction for bending (β = −1.4 unit) and a correction for parallelity of the ester chains of different molecules (1/2 ‖), are set forth in Table 2 $[P]_{calc.}$ II. Regarding esters of isostructure in Table 2, the corrections for bending in the isopropyl ester and for parallelity in the isobutyl ester of ethylphosphonous acid are assumed both for the main and the side chain*. As we see from the data of Table 2, the adoption of corrections for parallelity of the ester chains of two molecules leads to good agreement between the experimental and calculated parachors.

A second interesting problem concerns the possibility of the occurrence of association in monoesters of ethylphosphonous acids. From data for Raman spectra of lower dialkylphosphorous acids from dimethyl through dibutylphosphorous acids, A. E. Arbuzov, Batuev and Vinogradova [1] inferred the occurrence of association due to hydrogen bonding. Subsequently we arrived at the conclusion [6], on the basis of a study of the parachors of dialkylphosphorous acids, that the lower dialkylphosphorous acids were associated. The higher dialkylphosphorous acids, starting from dihexylphosphorous acid, proved to be monomeric. Association of dialkylphosphorous acids due to hydrogen bonds was confirmed by Meyrick and Thomson [7] by a study of the Raman and infrared spectra of dimethyl-, diethyl- and diisopropylphosphorous acids. Later, however, Bellamy and Beecher [8] did not confirm the data of Meyrick and Thomson for the infrared spectrum of diethylphosphorous acid.

We carried out [9] a cryoscopic measurement of the molecular weights of the dialkylphosphorous acids in benzene and showed that with increasing concentration the molecular weight of dimethylphosphorous acid rises, which indicates that dimethylphosphorous acid is associated in the liquid state [9]. Kosolapoff and Powell [10] point out that our data on rising molecular weights of lower dialkyphosphorous acids with increasing concentration were obtained for unusually high concentrations; on the basis of molecular weight determinations of diethyl and dibutyl-phosphorous acids in dilute solution, they consider them to be monomeric. Di-(p-di-methylaminophenyl) phosphorous acid was also found to be monomeric. Kosolapoff and McCullough [11] attempted to determine the susceptibility of dialkylphosphorous acids to hydrogen bond formation from their heats of mixing with chloroform.

TABLE 2

$C_2H_5P(OR)(OH)$	$[P]_{found}$	$[P]_{calc.}$ I β-correction	Deviation, in %	$[P]_{calc.}$ II	Correction	Deviation in %
CH_3	242.8	242.8	0	242.8	— —	0
C_2H_5	282.0	281.0	+ 0.4	281.0	−1.4 β	+ 0.4
n-C_3H_7	319.5	321.0	− 0.4	319.9	−2.5 β 1/2 ‖	− 0.1
i-C_3H_7	318.2	317.0	+ 0.4	317.0	−2.8 2β	+ 0.4
n-C_4H_9	359.6	361.1	− 0.4	358.8	−3.6 β 1/2 ‖ ·2	+ 0.2
i-C_4H_9	356.0	358.4	− 0.7	356.2	−3.6 β 1/2 ‖ ·2	0
C_6H_{13}	436.5	441.2	− 1.1	436.8	−5.8 β 1/2 ‖ ·4	0
C_7H_{15}	475.8	481.4	− 1.1	475.9	−6.9 β 1/2 ‖ ·5	0
C_8H_{17}	514.1	521.6	− 1.4	515.0	−8.0 β 1/2 ‖ ·6	− 0.1
C_9H_{19}	553.7	561.8	− 1.4	554.1	−9.1 β 1/2 ‖ ·7	0

We obtained data for the molecular weights of dialkylphosphorous acids both for low and unusually high concentrations. In the case of high concentrations these data must be considered carefully and should be regarded as evidence of only a tendency to increase of molecular weight. It must be pointed out that for associated liquids in a solvent (dioxan) which breaks the hydrogen bond of the investigated substances, the molecular weight does not rise appreciabley even up to a concentration of 8-9 moles per 100 moles solvent (acetic acid in dioxane [12].

It follows from what has been said that the problem of the association of dialkylphosphorous acids and closely related types of organic derivatives of phosphorus in the liquid state cannot be regarded as conclusively solved. For this reason, interest attaches to the study of the presence or absence of association in acid esters of ethylphosphonous

* The question of the need for corrections for the side chain cannot be said to be finally settled.

acid, since, in the opinion of Kosolapoff [11], substitution of the RO group by R directly linked to the phosphorus must increase the susceptibility to formation of a hydrogen bond.

In work with fatty acids Gibling [13] established the influence of association upon the magnitude of the molecular parachor. For higher fatty acids, associated to dimeric complexes, the difference in the value of the parachor, for each CH_2 group (Δ_{CH_2}) considerably exceeds the usual difference of 39.8 units. We carried out calculations of this type for the investigated esters, introducing corrections for interaction and without corrections. The difference obtained when corrections are introduced does not permit us to judge whether association of monoesters of ethylphosphonous acid occurs.

It is interesting to note that the group value of $C_2H_5P(O(C))OH$, calculated with corrections from the parachors of the nonyl and octyl esters (186.6 units), is very close to the value obtained from the parachor of the methyl ester. This also indicates the great probability of a monomeric form for esters of ethylphosphonous acid. The parachors calculated on the assumption of a dimeric form of the first members of the series, in the same way as for the dialkylphosphorous acids, do not give any indications of association of esters of ethylphosphonous acid.

We supplemented our data for the parachors of the monoesters of ethylphosphonous acid by carrying out cryoscopic measurements. In Table 3 are set forth the molecular weights determined in benzene solutions of various concentrations.

TABLE 3

$C_2H_5P(OR)OH$ theor. mol.wt.	Concentration (mole %)	Mol. wt. found	$C_2H_5P(OR)OH$ mol. wt. theor.	Concentration (mole %)	Mol. wt. found
C_2H_5 122.1	0.37	122.4	C_6H_{13} 178.2	0.27	181.6
	1.38	127.5		0.90	189.4
	2.06	129.7		1.67	194.5
	2.83	133.2		2.48	199.0
	4.41	135.7		3.77	199.8
n-C_3H_7 136.1	0.35	139.2	C_7H_{15} 192.2		
	1.18	144.9		0.36	190.4
	1.74	148.1		0.97	197.5
	2.60	151.2		1.95	198.9
	3.39	152.0		2.72	197.5
	4.65	153.8		3.34	197.6
n-C_4H_9 150.1	0.34	150.6	C_8H_{17} 206.2	0.16	203.4
	0.91	150.4		0.45	204.9
	2.27	155.4		0.93	211.5
	3.38	157.4		1.45	217.4
				2.15	221.2
				2.91	223.3
i-C_4H_9 150.1	0.31	150.0		3.58	220.7
	1.00	155.1			
	2.13	156.9	C_9H_{19} 220.3	0.26	221.4
	2.98	158.9		0.67	225.3
				0.93	227.0

As we see from Table 3, with rising concentration of the benzene solutions, in nearly all cases an insignificant rise of molecular weight is observed, not exceeding 10% of the monomeric molecular weight even at concentrations of 3-4 mole-%. However, on the basis of these data it is impossible to draw final conclusions about the absence of association in the lower monoesters of ethylphosphonous acid in the liquid state.

SUMMARY

1. Parachors of the series of monoesters of ethylphosphonous acid from methyl through nonyl have been found. There is good agreement between found and calculated parachors on the assumption of interaction of the chains of different molecules.

2. Data for parachors and molecular weights, the latter determined cryoscopically in benzene, point to monomeric forms of the esters examined rather than to their association.

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PARACHORS OF SOME ESTERS OF 5-NONANOL

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The method of group values proposed by Gibling [1] for calculation of the molecular parachor provides evidence of interaction of hydrocarbon chains of ester groups in esters of organic and inorganic acids, amines and other types of organic compounds both with the central atoms ("bending correction") and with one another ("correction for parallelity"). In the majority of compounds studied by the method of parachors, interaction of chains inside a molecule has been found, although recent parachor studies have given indications of interaction between the hydrocarbon chains of different molecules [2].

In applying the parachor method to the elucidation of structures of organic compounds, an unclarified aspect has been the corrections to be applied to molecular parachor values of compounds containing iso radicals. At the same time, branching of hydrocarbon radicals may exercise a considerable influence on a series of physical properties of organic compounds as clearly demonstrated, for example, in recent studies by Bradley, Mehrotra and Wardlaw [3] on alkoxyl derivatives of silicon, titanium and zirconium. Bradley Mehrotra and Wardlaw reach the conclusion that there is strong intermolecular interaction of the alkyl groups in these compounds.

In calculating the parachors of iso compounds with allowance for parallelity we may start from the consideration that either only the main chains interact with one another or there is also interaction with the side chains. A similar alternative may be considered in relation to the correction for chain bending. For esters of carbonic, malonic [1] and sulfurous acids [4] with branched chains, Gibling only applies a parallelity correction for the main chains.

In previous communications we presented calculations of the parachors of a series of iso esters with introduction of corrections for interaction between carbon atoms of both the main and the side chains. Misprints appeared in a table setting forth the calculated parachors of these esters with allowance for interaction also of the side chains [5]. We therefore reproduce this table again in Table 1 with the modification that the parachors of the isobutyl and isoamyl esters of malonic acid are calculated on the basis of a group value of $(C)OC\overset{O}{\overset{\|}{C}}H_2C\overset{O}{\overset{\|}{C}}O(C)$ 173.5 units; which value was found from the methyl ester with introduction of a correction of −2.2 units for parallelity of the carbons of the methyl groups.

As we see from Table 1, the data do not provide an answer to the question of the need to introduce corrections for the side chain, since no sharp difference in corrections is observed. In the majority of cases, however, the best results are got by introducing corrections for the side chain. Comparison of the parachors obtained for isopropyl phosphite [6] and isopropyl phosphate [5] with the parachors calculated with insertion of corrections for bending of all the β-carbon atoms of the ester chains showed good agreement.

On the assumption of parallelity of the two ester chains in esters of phosphorous acids [7], we calculated the parachor of triisobutyl phosphite:

	$[P]_{found}$	$[P]_{calc.}$	Deviation in %	Corrections
$i\text{-}(C_4H_9O)_3P$	610.2	612.4	− 0.3	− 8.63 β 2 ‖
		614.7	− 0.7	− 6.43 β 1 ‖

The data obtained also indicate the necessity to insert corrections for parallelity of the carbons of both the main and the side chains.

Gibling [4] derives the parachor of triisobutyl phosphate but does not apply corrections for branching of the ester chains; he assumes that the methyl radicals are arranged in the plane of symmetry of the PO_4 group so that corrections in this case should be of subsidiary importance. On the basis of data for ortho esters and acetals, Voronkov [8] concludes that corrections for parallelity in iso radicals need only be introduced for the main chains. Calculations of the parachors of the isopropyl and isoamyl esters of succinic and adipic acids * with allowance

* These parachors are enumerated in Vogel's paper [9].

TABLE 1

Name of compound	$[P]_{found}$	$[P]_{calc.}$	Deviation in %	Corrections
Diisobutyl carbonate	428.1	426.9	+ 0.3	− 4.4 2 ‖
		429.1	− 0.2	− 2.2 1 ‖
Diisoamyl carbonate	505.0	505.0	0	− 6.6 3 ‖
		507.2	− 0.4	− 4.4 2 ‖
Diisobutyl malonate*	511.8	511.3	0	− 8.8 4 ‖
		513.5	− 0.3	− 6.6 3 ‖
Diisoamyl malonate*	586.9	589.2	− 0.3	− 11.0 5 ‖
		591.4	− 0.7	− 8.8 4 ‖
Diisobutyl sulfite	450.6	449.0	+ 0.3	− 6.0 2 δ; 2 ‖
		451.2	− 0.1	− 3.8 2 δ; 1 ‖
Diisoamyl sulfite**	525.7	527.1	− 0.2	− 8.2 2 δ; 3 ‖
		529.3	− 0.7	− 6.0 2 δ; 3 ‖

* In paper [5] this was wrongly printed as diisoamyl sulfite.
** In the same paper this was printed as diisoamyl sulfate.

TABLE 2

Name of compound	$[P]_{found}$	$[P]_{calc.}$	Deviations (%)	Corrections
5-Nonyl acetate	491.2	493.1	− 0.3	− 1.4 2 δ
5-Nonyl carbonate	813.6	820.2	− 0.2	− 13.2 6 ‖
		826.9	− 0.8	− 6.6 3 ‖
5-Nonyl malonate	900.3	902.3	− 0.2	− 19.8 9 ‖
		911.1	− 1.2	− 11.0 5 ‖
Tetra(5-nonyl)silicate	1556.1	1566.8	− 0.6	− 46.4 8 γ 16 ‖
		1584.5	− 1.8	− 28.8 8 γ 8 ‖
Tri(5-nonyl) borate	1173.8*	1172.7	+ 0.1	− 30.4 6 γ 10 ‖
		1190.9	− 1.4	− 12.8 6 γ 2 ‖

* Calculated from γ and d_0, determined at 60°.

for parallelity of the main and side chains do not supply supplementary data. The difference in parachors in this case is 0.1-0.2% and lies within the limits of experimental error.

We see that inspection of the literature data for parachors of iso compounds does not lead to a decisive answer to the question of corrections. For the purpose of obtaining supplementary data, we synthesized esters of 5-nonanol in which the differences in corrections are large and more conspicuous. In Table 2 the data that we obtained for the parachors of 5-nonyl esters are compared with the theoretical values calculated for two possible structures: assumption of interaction of carbon atoms of only the main chains and introduction of corrections for interaction of both the main and the side chains.

Assuming a paired arrangement of ester chains in orthosilicates [10] and their branching in the 5-nonyl radical, the corrections for parallelity are taken as 4 ‖ for the δ-carbon and 4 ‖ for the ε-carbon for each pair of 5-nonyl chains, giving a total of 16 ‖ for the molecule of tetra(dibutylcarbinyl) silicate. The parachor of 5-nonyl borate, calculated with allowance for interaction of the side chains, includes a correction for parallelity for the δ- and ε-carbons of the two 5-nonyl chains arranged on one side of the BO_3 group (8 ‖) and for the δ- and ε-carbons of the third branched chain located on the other side of the BO_3 group (2 ‖) [11].

The data set forth in Table 2 conclusively point to the necessity for insertion of corrections for parallelity of the side chains. The errors resulting from allowance of corrections only for the main chains reach 0.8-1.5%. Parachors obtained for compounds containing branched chains are lower in the majority of cases than the parachors of their normal-chain isomers. Thus, for example, the parachor of the tetranonyl ester of orthosilicic acid is 1591.8 units [10] and differs from the parachor of tetra(5-nonyl)-silicate by 35.7 units. The difference, however, in the group values of these esters is only 10.4 units. Consequently the 25.3 units of difference in the parachors must be attributed to the corrections which are introduced to allow for the structural differences between esters with branched and unbranched chains.

EXPERIMENTAL

5-Nonanol was prepared by the method of [12] and had b.p. 88-88.5° (13 mm).

5-Nonyl carbonate was prepared by transesterification of diethyl carbonate, using 12 g 5-nonanol and 4 g ethyl carbonate. The reaction was carried out in a flask with a Widmer column in presence of metallic sodium as catalyst. Two distillations gave a pure product (4 g) with b.p. 156-156.5° (3.5 mm); n_D^{20} 1.4330; d_4^{20} 0.8765; γ^{20} 27.1 dynes/cm.

	Found %:	C 72.62; H 12.18
$C_{19}H_{38}O_3$.	Calculated %:	C 72.56; H 12.17

5-Nonyl acetate. From 10 g 5-nonanol and 5.5 g acetyl chloride was obtained 9 g 5-nonyl acetate with b.p. 206-207° (754 mm); n_D^{20} 1.4205; d_4^{20} 0.8577; γ^{20} 26.2 dynes/cm [13].

5-Nonyl malonate was obtained by transesterification of diethyl malonate (5.5 g) with 5-nonanol (10 g) in presence of metallic sodium (pellets). Ethyl alcohol came off with difficulty at a bath temperature of 80-115°. 4 ml alcohol came over. Two distillations gave 5 g product with b.p. 192-193° (7.5 mm); n_D^{20} 1.4415; d_4^{20} 0.9156; γ^{20} 28.5.

	Found %:	C 70.30; H 11.11
$C_{21}H_{40}O_4$.	Calculated %:	C 70.74; H 11.31

Tri(5-nonyl) borate. Reactants were 7 g tri-n-butyl borate and 15 g 5-nonanol. The butyl alcohol came off at a bath temperature of 180°. 7 ml of the alcohol was collected (theoretical requirement 6.6 g). The bath temperature at the close of distillation of the alcohol was 240°. Two distillations gave a rapidly crystallizing product with b.p. 167° (1.5 mm); d_4^{60} 0.8159; γ^{60} 22.33; m.p. 55-56°.

	Found %:	B 2.45
$C_{27}H_{57}O_3B$.	Calculated %:	B 2.45

Tetra(5-nonyl) silicate was prepared by transesterification of tetraethyl orthosilicate (6 g) with 5-nonanol (16 g). The reaction takes place on adding a small pellet of sodium. 5.2 ml alcohol came off (5.5 g theoretical amount) at a bath temperature of 250°. On vacuum distillation, 2 g 5-nonanol (73-75°, 5 mm) was recovered and 9 g ester was obtained with b.p. 200-201° (1 mm); n_D^{20} 1.4395; d_4^{20} 0.8718, γ^{20} 26.6.

	Found %:	C 72.06; H 12.56
$C_{36}H_{76}O_4Si$.	Calculated %:	C 71.94; H 12.74

SUMMARY

1. The 5-nonyl esters of carbonic, malonic, boric and orthosilicic acids, not previously described in the literature, were synthesized.

2. The parachors that we obtained indicate the necessity for corrections for the parallelity of the main and side chains.

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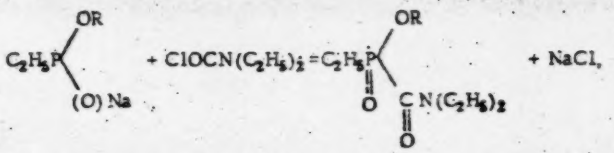
ETHYLPHOSPHONOUS ESTERS AND SOME OF THEIR TRANSFORMATIONS

COMMUNICATION 4. SYNTHESIS OF ESTERS OF ETHYLDIETHYLAMIDOFORMYLPHOSPHONIC ACID

B. A. Arbuzov and N. I. Rizpolozhensky

In the preceding paper [1] we described the synthesis of diethylamides of esters of phosphonoformic acid. In the course of study of the properties of esters of ethylphosphonous acid (full) and of partial esters of ethylphosphonous acid synthesized by us [2], we prepared a series of esters of ethyldiethylamidoformylphosphonic acid. These esters, like the diethylamides of the esters of phosphonoformic acid, were prepared by two methods. We have previously described [4] one of the methods of preparation of esters of ethyldiethylamidoformylphosphonous acid – the A. E. Arbuzov rearrangement [3] of full esters of ethylphosphonous acid with diethylcarbamyl chloride.

In the present paper we describe a synthesis of esters of ethyldiethylamidoformylphosphonic acid by the action of diethylcarbamyl chloride on the sodium salts of esters of ethylphosphonous acid [5]:



where R = C_2H_5-; n-C_3H_7-; i-C_3H_7-; n-C_4H_9-; i-C_4H_9-;

n-$C_6H_{13}-$; n-$C_7H_{15}-$; n-$C_8H_{17}-$; n-$C_9H_{19}-$; n-$C_{10}H_{21}-$;

It must be pointed out that the yield of esters of ethyldiethylamidoformylphosphonic acid is lower in this case than in rearrangement of the full esters of ethylphosphonous acid by diethylcarbamyl chloride.

The physical properties of the esters prepared are set forth in Table 1.

It may be noted that on examining the table of physical properties the measured molecular refraction is seen to differ from the calculated value by approximately a constant amount, 1.37 on the average. This indicates that for esters of the structure in question the value of the atomic refraction of nitrogen and phosphorus should have differed from the value adopted by us in calculating the molecular refraction.

For the atomic refraction of phosphorus we took the value of 4.27° [6]. For the AR of nitrogen we took 2.49 [7]. The remaining values of atomic refractions were those given by Eisenlohr.

EXPERIMENTAL

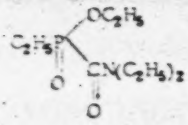
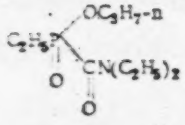
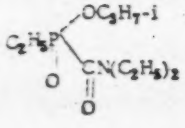
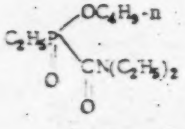
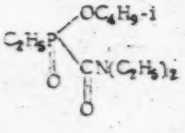
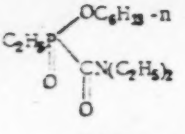
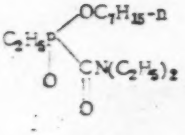
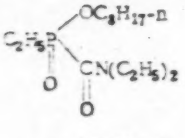
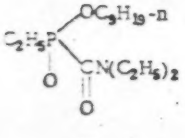
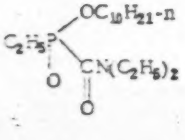
Synthesis of ethyl ester of ethyldiethylamidoformylphosphonic acid. Into a 3-necked flask fitted with stirrer, reflux condenser and dropping funnel were introduced 1 g sodium (excess of 0.3 g) and about 80 ml ether. 4 g ethyl ester of ethylphosphonous acid was then run in. The flask was heated for 2 hours on a water bath. The excess of sodium was eliminated and into the ethereal solution of the sodium salt of the ethyl ester of ethylphosphonous acid was run (through the dropping funnel) 4.3 g diethylcarbamyl chloride, after which the flask was heated for an hour on the water bath. The precipitate of sodium chloride was separated by centrifuging and the residue (after removal of the ether) was distilled in vacuum from an Arbuzov flask.

Two fractional distillations from the Arbuzov flask yielded the ethyl ester of ethyldiethylamidoformylphosphonic acid with the following constants: b.p. 107-108° (2 mm); d_4^{20} 1.0538; n_D^{20} 1.4630; found MR 57.82; calculated for $C_9H_{20}O_3PN$ MR 56.59; yield 2.9 g, or 40% of theoretical.

$C_9H_{20}O_3PN$. Found %: P 13.85; 13.92
Calculated %: P 14.03

In all the following experiments the same procedure was used for the syntheses.

TABLE 1

Formula of ester	B.p. in °C (p in mm Hg column)		d_4^{20}	n_D^{20}	MR found	MR calculated	Yield in %
	107-108	(2)	1.0538	1.4630	57.82	56.59	40
	112-113	(2)	1.0346	1.4622	62.54	61.21	36.8
	133-134	(9)	1.0286	1.4595	62.58	61.21	35.1
	111-112	(0.5)	1.0208	1.4625	67.20	65.82	42.3
	145-146.5	(9)	1.0170	1.4610	67.26	65.82	45.7
	131-132	(2.5)	0.9725	1.4500	76.65	75.05	34.8
	143-145	(2)	0.9817	1.4565	80.75	79.67	30
	137-138	(0.5)	0.9782	1.4618	85.80	84.29	42
	145-147	(1.5)	0.9702	1.4612	90.38	88.91	55
	160-162	(1.5)	0.9630	1.4600	94.84	93.52	53.5

Synthesis of n-propyl ester of ethyldiethylamidoformylphosphonic acid. Reactants were 3.8 g n-propyl ester of ethylphosphonous acid, 0.7 g sodium (with excess) and 3.8 g diethylcarbamyl chloride. The ester obtained had the constants: b.p. 112-113° (2 mm); d_4^{20} 1.0346; n_D^{20} 1.4622; found MR 62.54; calculated for $C_{10}H_{22}O_3PN$ MR 61.21; yield 2.4 g, or 36.8% of theoretical.

	Found %:	P 13.12; 13.26
$C_{10}H_{22}O_3PN$.	Calculated %:	P 13.19

Synthesis of isopropyl ester of ethyldiethylamidoformylphosphonic acid. Reactants were 0.6 g sodium (with excess), 2.5 g isopropyl ester of ethylphosphonous acid and 2.5 g diethylcarbamyl chloride. The isopropyl ester of ethyldiethylamidoformylphosphonic acid had the following constants: b.p. 133-134° (9 mm); d_4^{20} 1.0286, n_D^{20} 1.4595; Found MR 62.58; calculated for $C_{10}H_{22}O_3PN$. MR 61.21, yeild of ester 1.5 g, or 35% of the theoretical.

	Found %:	P 13.12; 13.00
$C_2H_{22}O_3PN$.	Calculated %:	P 13.19

Preparation of n-butyl ester of ethyldiethylamidoformylphosphonic acid. Reactants were 1.5 g sodium (with excess), 6.0 g butyl ester of ethylphosphonous acid, 5.4 g diethylcarbamyl chloride. The n-butyl ester of ethyldiethylamidoformylphosphonic acid had the following constants: b.p. 111-112° (0.5 mm); d_4^{20} 1.0208; n_D^{20} 1.4625; found MR 67.20; calculated for $C_{11}H_{24}O_3PN$ MR 65.82; yield 4.2 g, or 42.3% of theoretical.

	Found %:	P 12.41; 12.55
$C_{17}H_{24}O_3PN$.	Calculated %:	P 12.42

Preparation of isobutyl ester of ethyldiethylamidoformylphosphonic acid. Reactants were 1 g sodium (with excess), 4.2 g isobutyl ester of ethylphosphonous acid and 3.8 g diethylcarbamyl chloride. The isobutyl ester of ethyldiethylamidoformylphosphonic acid was obtained in a yield of 3.2 g or 45.7% of the theoretical. Constants: b.p. 145-146.5° (9 mm); d_4^{20} 1.0170; n_D^{20} 1.4610; found MR 67.26; calculated for $C_{11}H_{24}O_3PN$ MR 65.82.

	Found %:	P 12.25; 12.33
$C_{11}H_{24}O_3PN$.	Calculated %:	P 12.42

Synthesis of n-hexyl ester of ethyldiethylamidoformylphosphonic acid. Reactants were 1.4 g sodium (with excess), 7.2 g n-hexyl ester of ethylphosphonous acid and 5.5 g diethylcarbamyl chloride. The hexyl ester of ethyldiethylamidoformylphosphonic acid was obtained in the amount of 3.9 g or 34.8% of the theoretical b.p. 131-132° (2.5 mm); d_4^{20} 0.9725; n_D^{20} 1.4565; found MR 76.65; calculated for $C_{13}H_{28}O_3PN$ MR 75.05.

	Found %:	P 11.02; 10.95
$C_{13}H_{28}O_3PN$.	Calculated %:	P 11.18

Synthesis of n-heptyl ester of ethyldiethylamidoformylphosphonic acid. Reactants were 1 g sodium (with excess), 5.5 g n-heptyl ester of ethylphosphonous acid and 3.9 g diethylcarbomyl chloride. The heptyl ester of ethyldiethylamido formylphosphonic acid was obtained in amount of 2.5 g or 30% of the theoretical: b.p. 143-145° (2 mm); d_4^{20} 0.9817; n_D^{20} 1.4565, found MR 80.75; calculated for $C_{14}H_{30}O_3PN$ MR 79.67.

	Found %:	P 10.67; 10.69
$C_{14}H_{30}O_3PN$.	Calculated %:	P 10.65

Synthesis of n-octyl ester of ethyldiethylamidoformylphosphonic acid. Materials used were 1 g sodium (with excess), 5.3 g n-octyl ester of ethylphosphonous acid and 3.5 g diethylcarbamyl chloride. The n-octyl ester of ethyldiethylamidoformylphosphonic acid had the following constants: b.p. 137-138°(0.5 mm) d_4^{20} 0.9782, n_D^{20} 1.4618; found MR 85.80, calculated for $C_{15}H_{32}O_3PN$ MR 84.29; yield of ester 3.5 g, or 42% of theoretical.

	Found %:	P 10.36; 10.28
$C_{15}H_{32}O_3PN$.	Calculated %:	P 10.18

Synthesis of n-nonyl ester of ethyldiethylamidoformylphosphonic acid. The synthesis was performed with 1.5 g sodium (with excess), 7.2 g n-nonyl ester of ethylphosphonous acid and 4.5 g diethylcarbamyl chloride. Fractional distillation of the reaction products in vacuum from an Arbuzov flask gave the n-nonyl ester with the following constants: b.p. 145-147° (1.5 mm); d_4^{20} 0.9702; n_D^{20} 1.4612; found MR 90.38, calculated for $C_{16}H_{32}O_3PN$ MR 88.91; yield 5.8 g or 55% of theory.

	Found %:	P 9.65; 9.61
$C_{16}H_{32}O_3PN$	Calculated %:	P 9.73

Synthesis of n-decyl ester of ethyldiethylamidoformylphosphonic acid. Synthesis was performed with 1 g sodium (with excess), 6 g decyl ester of ethylphosphonous acid and 3.5 g diethylcarbamyl chloride. Vacuum fractionation from an Arbuzov flask gave the n-decyl ester of ethyldiethylamidoformylphosphonic acid with the following constants: 160-162° (1.5 mm); d_4^{20} 0.9630; n_D^{20} 1.4603; found MR 94.84; calculated for $C_{17}H_{34}O_3PN$ MR 93.52; yield 4.6 g, or 53.5% of theory.

	Found %:	P 9.32; 9.28
$C_{17}H_{34}O_3PN$.	Calculated %:	P 9.3

SUMMARY

Reaction of diethylcarbamyl chloride with the sodium salts of the partial esters of ethylphosphonous acid gave esters of ethyldiethylamidoformylphosphonic acid.

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* See Consultants Bureau Translation, page 759.
** See Consultants Bureau Translation, page 843.
*** See Consultants Bureau Translation, page 765.

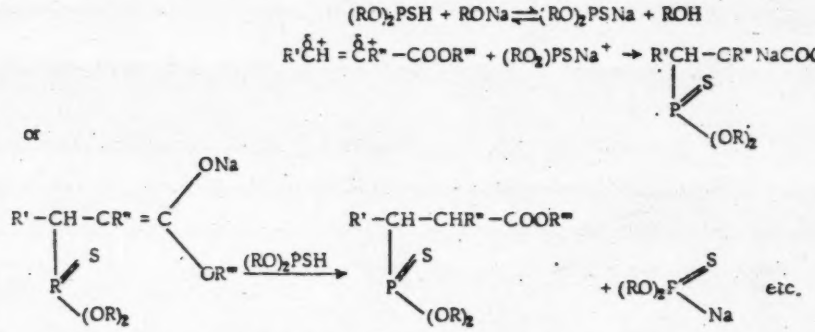
NEW METHOD OF SYNTHESIS OF ESTERS OF PHOSPHONIC AND THIOPHOSPHONIC ACIDS

16. SYNTHESIS OF ESTERS OF MONO-, DIPHOSPHONO-, AND THIO- PHOSPHONOCARBOXYLIC ACIDS

A. N. Pudovik and D. Kh. Yarmukhametova

As one of us has shown, in the presence of alcoholates of alkali metals the dialkylphosphorous acids very easily add on to esters of unsaturated mono- and dibasic acids and ketocarboxylic acids [1], unsaturated nitriles [2], aldehydes [3] and ketones [4], vinyl acetate [5] and imines [6] with formation, respectively, of esters of phosphonocarboxylic acids their nitriles and amines, esters of ketophosphonic and unsaturated hydroxyphosphonic esters, esters of phosphoethyl acetate, substituted aminophosphonic esters, etc. Esters of unsaturated carboxylic acids used in reactions with dialkylphosphorous acids were esters of acrylic, methacrylic, crotonic, cinnamic, maleic and acetylenedicarboxylic acids. In the majority of cases the esters of phosphonocarboxylic acids were obtained in high yields.

Recently, Kabachnik and Mastryukova described the synthesis of dialkylthiophosphorous acids [7]. Dialkylthiophosphorous acids were also prepared in our laboratory in 1950-1951 by Nikonorov and one of us and used for the synthesis of esters of ketothiophosphonic and unsaturated hydroxythiophosphonic acids [8]. In continuation of these investigations, it appeared to us of interest to undertake the addition of dialkylthiophosphorous acids to esters of unsaturated carboxylic acids, to synthesize previously unknown esters of thiophosphonocarboxylic acids and to study their properties. The addition was performed in presence of sodium alkoxides. The course of the reactions may be represented by the following scheme:



where R = C_2H_5, n- C_3H_7, n- C_4H_9, i- C_4H_9; R' = H, CH_3, C_6H_5, COOR'''; R'' = H, CH_3; R''' = CH_3, C_2H_5, n- C_3H_7, iso-C_4H_9, n- C_4H_9.

It should be noted that when carrying out the addition of dialkylthiophosphorous acids to esters of unsaturated acids containing different radicals in the carboxyl groups, it was not possible in all cases, due to transesterification, to obtain completely pure products. Esters of thiophosphonocarboxylic acids were synthesized in the pure form when using dialkylthiophosphorous acids, esters of carboxylic acids and alkoxides of alcohols with identical radicals in the alkoxyl and carboxyl groups. The constants and yields of the resultant esters of dialkylthiophosphonocarboxylic acids are set forth in Table 1.

We see that the esters of thiophosphonopropionic, thiophosphonoisobutyric, thiophosphonophenylpropionic, thiophosphonosuccinic acids were obtained in quite high yields.

Hydrolysis of the methyl ester of β-(diethylthiophospho)-propionic acid gave an acid with m.p. 162-162.5°. A strong odor of hydrogen sulfide was noticed when the tube was opened and the solution evaporated. Analysis of

this acid showed it to be free from sulfur. Analysis for phosphorus gave results very close to the theoretical requirement for β-phosphonopropionic acid. A. E. Arbuzov gave m.p. 166-166.5° for β-phosphonopropionic acid. A mixed sample of the acid obtained by hydrolysis of the ester of β-(diethylthiophosphono) propionic acid with the β-phosphonothiopropionic acid synthesized by hydrolysis of the ester of β-(diethylphosphono)-propionic acid melted at 162-163°.

TABLE 1

No.	Formula	B.p. in °C (pressure in mm Hg)	d_4^{25}	n_D^{25}	Yield in %
1	$(C_2H_5O)_2P(=S)-CH_2CH_2COOCH_3$	110 (1.5)	1.1225	1.4652	86
2	$(C_2H_5O)_2P(=S)-CH_2CH(CH_3)-COOCH_3$	98–98.5 (0.5)	1.0975	1.4646	88
3	$(C_3H_7O)_2P(=S)-CH_2-CH(CH_3)-COOC_3H_7$	136–136.5 (1)	1.0340	1.4630	83
4	$(C_4H_9O)_2P(=S)-CH_2-CH(CH_3)-COOC_4H_9$-n	159 (0.5)	1.0061	1.4600	81
5	$(i\text{-}C_4H_9O)_2P(=S)-CH_2-CH(CH_3)-COOC_4H_9$-i	145 (1)	1.0000	1.4600	70
6	$(C_2H_5O)_2P(=SCH_3)-CH-CH_2COOC_2H_5$	108–109 (1)	1.0777	1.4612	80
7	$(C_2H_5O)_2P(=S)-CH(C_6H_5)-CH_2-COOC_2H_5$	158.5 (1)	1.1278	1.5112	76
8	$(C_2H_5O)_2P(=S)-CH(COOC_2H_5)-CH_2-COOC_2H_5$	146.5 (1)	1.1319	1.4630	78

Consequently the process of hydrolysis of the ester of β-(diethylthiophosphono) propionic acid proceeds with cleavage of sulfur from the thiophospho group and its substitution by oxygen

$$(RO)_2P(=S)-CH_2CH_2COOR \xrightarrow[H_2O]{2HCl} (HO)_2P(=O)-CH_2CH_2COOH + 2RCl + ROH + H_2S.$$

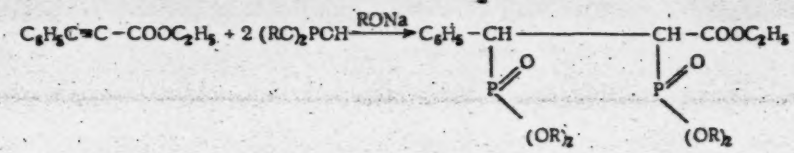
In order to obtain confirmation that the cleavage of sulfur from the thiophosphono group, proceeding during hydrolysis of the ester of β-(diethylthiophosphono)-propionic acid is not fortuitous, the ethyl ester of ethylthiophosphonic acid was synthesized and then hydrolyzed. In this case also, although less easily and less completely, cleavage of sulfur was effected.

In one of our previous investigations it was shown [1] that acid esters of ethyl- and phenylphosphonous acid readily add on to esters of acrylic and methacrylic acids with formation of esters of the corresponding carboxyalkylphosphonic acids. In a similar manner we synthesized the products of addition of the above acids to the esters of crotonic, cinnamic and maleic acids. The constants and yields of the synthesized esters of carboxyethylphosphonic acids are set forth in Table 2.

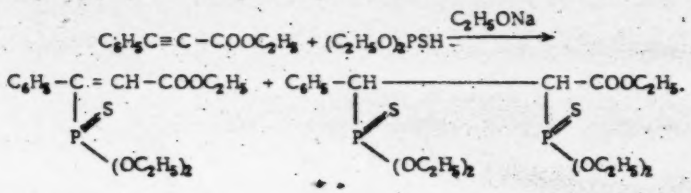
Hydrolysis of these esters gave: α-methyl-β-carboxydiethylphosphonic acid with m.p. 82-82.5°; α-phenyl-β-carboxydiethylphosphonic acid with m.p. 138-138.5°; and α,β-dicarboxydiethylphosphonic acid with m.p. 131-131.5°

Interesting results were obtained by addition of esters of phosphorus acids to esters of phenylpropiolic acid. Addition of dimethylphosphorous and diethylphosphorous acids to the methyl and ethyl esters of phenylpropiolic acid, both when using equimolar ratios of reactants and when using an excess of the dialkylphosphorous acids, gives in the pure form only esters of diphosphonophenylpropionic acid. The structure of the addition products has not been

rigorously established, but it is most probable that their phosphono groups are located at both of the carbon atoms:



Hydrolysis of the product of addition of diethylphosphorous acid to the methyl ester of phenylpropiolic acid gave diphosphonophenylpropionic acid with m.p. 113-115°. Addition of diethylthiophosphorous acid to the ethyl ester of phenylpropiolic acid yielded products of addition of both one and two molecules of acid:



On addition of the ethyl ester of ethylphosphonous acid to the ethyl ester of phenylpropiolic acid, we succeeded in isolating only the product of addition of one molecule of the acid ester. Diethylthiophosphorous acid adds on with great facility to the diethyl ester of acetylenedicarboxylic acid, the main product of reaction being that of the addition of two molecules of acid:

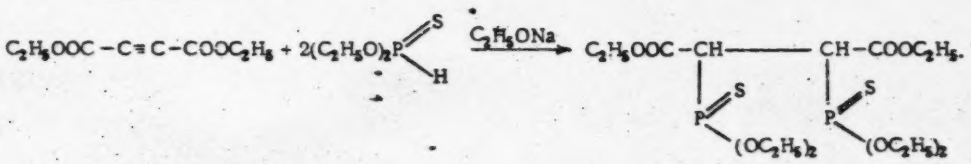
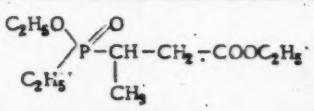
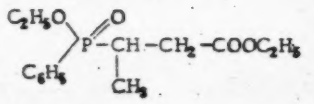
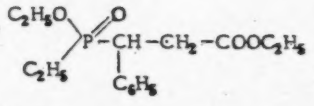
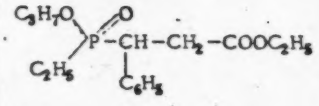
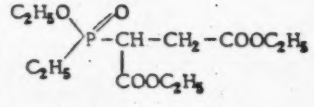
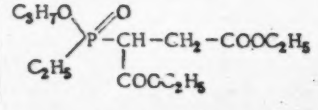


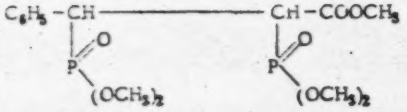
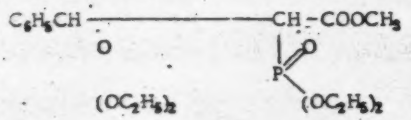
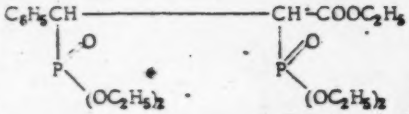
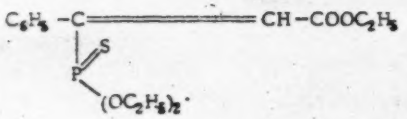
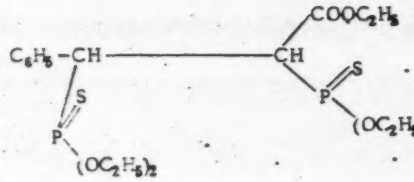
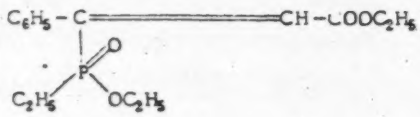
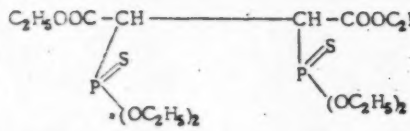
TABLE 2

No.	Formula	B.p. in °C (pressure in mm mercury)	n_D^{20}	d_4^{20}	Yield in %
1		118-120 (1.5)	1.4492	1.0564	78
2		154-155 (1.5)	1.5025	1.1128	77
3		157-158 (0.5)	1.5040	1.1048	76
4		164-166 (1)	1.5012	1.0844	69
5		142 (1)	1.4481	1.1142	60
6		151-152.5 (0.5)	1.4510	1.1015	57

In spite of repeated fractionation it was not possible to isolate products of addition of one molecule from the lower boiling fractions. The constants and yields of the esters of carboxyalkylphosphonic and thiophosphonic acids obtained by addition of dialkylphosphorous and dialkylthiphosphorous acids, also these of the addit on of the ethyl ester of ethylphosphonous acid to esters of phenylpropiolic and acetylenedicarboxylic acids, are set forth in Table 3.

The products of addition of two molecules of diethylphosphorous and diethylthiophosphorous acids to esters of phenylpropiolic and acetylene dicarboxylic are very viscous liquids, readily soluble in alcohol and ether, insoluble in water.

TABLE 3

No.	Formula	B. P. in °C (pressure in mm mercury)	n_D^{20}	d_4^{20}	Yield in %
1		210-212 (4)	1.5072	–	46
2		208 (2)	1.4939	1.2086	50
3		202 (0.5)	1.4915	1.1754	47
4		168-169 (1)	1.5369	1.1534	32
5		212 (1)	1.5271	–	15
6		147-148 (0.5)	1.5082	1.1054	30
7		185 (1)	1.4885	1.1890	21

EXPERIMENTAL

Addition of diethylthiophosphorous acid to methyl acrylate. To a reaction mixture comprising 8.5 g of diethylthiophosphorous acid and 4.8 g of methyl acrylate was slowly added, dropwise, a concentrated solution of sodium ethylate in absolute ethyl alcohol. Considerable heat was developed during the reaction. The solution of sodium ethylate was added until the mixture ceased to evolve heat; a total of about 10 drops was added. The reaction mixture was heated on the water bath for 2 hours. Fractionation gave 12 g of the methyl ester of β-diethylthiophosphonopropionic acid (Table 1, compound 1) and (at the bottom of the flask) a small quantity of resin.

Found %: P 13.17; 13.24

$C_8H_{17}O_4PS$. Calculated %: P 12.92

Hydrolysis of the methyl ester of β-diethylthiophosphonopropionic acid. 4.3 g ester was heated with 45 ml dilute (1:1) HCl in a sealed tube at 130-140° for 8 hours. On opening the tube a strong odor of hydrogen sulfide was noticed. After repeated evaporation of the mixture with periodic replenishing with distilled water the hydrochloric acid and hydrogen sulfide were driven off. Further evaporation of the solution resulted in deposition of crystals which after three recrystallizations from water and drying in the air melted at 162-162.5°.

Found %: P 20.24; 20.20

$C_3H_7O_4SP$. Calculated %: P 18.23

$C_3H_7O_3P$ Calculated %: P 20.13

Analysis for sulfur gave a negative result. A mixed sample with synthetic β-phosphonopropionic acid did not give a depression of melting point.

Addition of diethylthiophosphorous acid to methylmethacrylate. The reaction was carried out with 6.6 g diethylthiophosphorous acid and 4.3 g methyl methacrylate in presence of sodium ethylate. There was obtained 9.6 g methyl ester of α-methyl-β-diethylthiophosphonopropionic acid (Table 1, compound 2).

Found %: P 12.51

$C_9H_{19}O_4PS$. Calculated %: P 12.21

Addition of dipropylthiophosphorous acid to propyl methacrylate. Reactants were 5.3 g dipropylthiophosphorous acid and 3.7 g propyl methacrylate. The reaction was performed in presence of sodium propylate. There was obtained 6.8 g propyl ester of α-methyl-β-dipropylthiophosphonopropionic acid (Table 1, compound 3).

Found % P 10.19; 10.29

$C_{13}H_{27}O_4PS$. Calculated %: P 10.00

Addition of dibutylthiophosphorous acid to butyl methacrylate. Reactants were 4.1 g dibutylthiophosphorous acid and 2.8 g butyl methacrylate in presence of sodium butylate. 5.6 g butyl ester of α-methyl-β-dibutylthiophosphonopropionic acid was obtained (Table 1, compound 4).

Found %: P 9.17; 9.23

$C_{16}H_{33}O_4PS$. Calculated %: P 8.81

Addition of diisobutylthiophosphorous acid to isobutyl methacrylate. Reaction was effected between 3.5 g diisobutylthiophosphorous acid and 2.4 g isobutyl methacrylate in presence of sodium isobutylate. 4.2 g isobutyl ester of α-methyl-β-diisobutylthiophosphonopropionic acid was obtained (Table 1, compound 5).

Found %: P 9.22; 9.11

$C_{16}H_{33}O_4PS$. Calculated %: P 8.81

Addition of diethylthiophosphorous acid to ethyl crotonate. Reactants were 4.6 g diethylthiophosphorous acid and 3.4 g ethyl crotonate. Yield 6.1 g of the ethyl ester of β-methyl-β-diethylthiophosphonopropionic acid (Table 1, compound 6).

Found %: P 11.68; 11.64

$C_{10}H_{21}O_4PS$. Calculated %: P 11.57

Addition of diethylthiophosphorous acid to ethyl cinnamate. 3 g diethylthiophosphorous acid was reacted with 3.3 g ethyl cinnamate in presence of sodium ethylate. 5.2 g ethyl ester of β-phenyl-β-diethylthiophosphonopropionic acid was obtained (Table 1, compound 7).

Found %: P 9.57; 9.70

$C_{15}H_{23}O_4PS$. Calculated %: P 9.39

Addition of diethylthiophosphorous acid to diethyl maleate. 2.5 g diethylthiophosphorous acid was reacted with 2.8 g diethyl maleate in presence of sodium ethylate to give 4.1 g diethyl ester of diethylthiophosphonosuccinic acid (Table 1, compound 8).

Found %: P 9.75; 9.68

$C_{12}H_{23}O_6PS$. Calculated %: P 9.51

Addition of ethyl ester of ethylphosphonous acid to ethyl crotonate. Reaction between 2.6 g ethyl ester of ethylphosphonous acid and 2.4 g ethyl crotonate in presence of sodium ethoxide gave 3.7 g ethyl ester of α-methyl-β-(carboxyethyl)-diethylphosphonic acid (Table 2, compound 1).

Found %: P 13.22; 13.40

$C_{10}H_{21}O_4P$. Calculated %: P 13 14

Addition of ethyl ester of phenylphosphonous acid to ethyl crotonate. Reaction between 3.9 g ethyl ester of phenylphosphonous acid and 2.6 g ethyl crotonate in presence of sodium ethylate gave 5 g ethyl ester of α-methyl- β-(carboxyethyl)-ethyl-phenylphosphonic acid (Table 2, compound 2).

Found %: P 10.91

$C_{14}H_{21}O_4P$. Calculated %: P 10.91

Hydrolysis of ethyl ester of α-methyl- β-(carboxyethyl)-ethylphosphonic acid. 4.1 g ester was heated with 4 ml dilute HCl (1:1) in a sealed tube at 140° for 8 hours. After repeated evaporation with periodic addition of water to the reaction mixture and final evaporation, 2.3 g crystals came down. After three recrystallizations from water, pure α-methyl-β-carboxydiethylphosphonic acid was obtained with m.p. 82-82.5°. Yield 1.5 g or 70 % of the theoretical.

Found %: P 13.33

$C_6H_{13}O_4P$. Calculated %: P 13.59

Addition of ethyl ester of ethylphosphonous acid to ethyl cinnamate. Reaction of 3.9 g ethyl ester of ethylphosphonous acid with 5.7 g ethyl cinnamate gave 7.3 g ethyl ester of α-phenyl- β-(carboxyethyl)-diethylphosphonic acid (Table 2, compound 3).

Found %: P 10.49

$C_{15}H_{23}O_4P$. Calculated %: P 10.40

Hydrolysis of ethyl ester of α-phenyl- β-(carboxyethyl)-diethylphosphonic acid. 4.9 g ester was heated with 40 ml dilute HCl (1:1) in a sealed tube at 140° for 8 hours. After repeated evaporation with periodic addition of water to the reaction mixture followed by a final evaporation, 3.2 g crystals came down. After two recrystallizations from water, they melted at 138-138.5°. Yield 82% of theoretical.

Found %: P 12.66

$C_{11}H_{15}O_4P$. Calculated %: P 12.80

Addition of n-propyl ester of ethylphosphonous acid to ethyl cinnamate. Reaction between 2.4 g n-propyl ester of ethylphosphonous acid and 3.1 g ethyl cinnamate in presence of sodium propylate gave 3.8 g n-propyl ester of α-phenyl-β-(carboxyethyl)-diethylphosphonic acid (Table 2, compound 4).

Found %: P 9.79; 9.88

$C_{16}H_{25}O_4P$. Calculated %: P 9.93

Addition of ethyl ester of ethylphosphonous acid to diethyl maleate. Reaction between 2.1 g ethyl ester of ethylphosphonous acid and 3 g diethyl maleate gave 3 g ethyl ester of α, β-di(carboxyethyl)-diethylphosphonic acid (Table 2, compound 5).

Found %: P 10.46; 10.54

$C_{12}H_{23}O_6P$ Calculated %: P 10.56

Addition of n-propyl ester of ethylphosphonous acid to diethyl maleate. Reaction between 2.5 g n-propyl ester of ethylphosphonous acid and 3.15 g diethyl maleate in presence of sodium ethylate gave 3.2 g n-propyl ester of α,β-di(carboxyethyl)-diethylphosphonic acid (Table 2, compound 6).

Found %: P 9.90; 9.93

$C_{13}H_{25}O_6P$. Calculated %: P 10.06

Hydrolysis of n-propyl ester of α,β-di(carboxyethyl)-diethylphosphonic acid. 6 g ester was heated with 40 ml dilute HCl (1:1) in a sealed tube at 140° for 8 hours. After repeated evaporation of the reaction mixture with periodic addition of distilled water, final evaporation gave 3 g crystals. These could not be recrystallized from water or other solvents. The crystals were thoroughly washed with methyl-ethyl ketone. M.p. of crystals 131-131.5°. Yield of acid 75 % of theoretical.

Found %: P 14.67

$C_6H_{11}O_6P$. Calculated %: P 14.76

Addition of dimethylphosphorous acid to methyl phenylpropiolate. Reaction between 6.2 g dimethylphosphorous acid and 10 g methyl phenylpropiolate in presence of sodium ethoxide gave 7.3 g methyl ester of α, β-di-(dimethylphosphono)-phenylpropionic acid (Table 3, compound 1). The compound crystallized on standing. After recrystallization from benzene the crystals melted at 109-111°.

Found %: P 16.24; 16.37

$C_{14}H_{22}O_3P_2$. Calculated %: P 16.32

Addition of diethylphosphorous acid to methyl phenylpropiolate. Reaction between 14.6 g diethylphosphorous acid and 7.5 g methyl phenylpropiolate in presence of sodium ethylate gave 12.5 g methyl ester of α,β-di-(diethylphosphono)-phenylpropionic acid (Table 3, compound 2).

Found %: P 14.02; 13.98

$C_{12}H_{25}O_5P_2$. Calculated %: P 14.24

Hydrolysis of methyl ester of α, β-di-(diethylphosphono)-phenylpropionic acid. 4.5 g ester was heated in a tube with dilute HCl (1:1) for 6 hours at 130°. After repeated evaporation with fresh quantities of water, final evaporation gave crystals with m. p. 113 -115°.

Found %: P 19.8; 19.95

$C_9H_{12}O_5P_2$. Calculated %: P 20.00

Addition of diethylphosphorous acid to ethyl phenylpropiolate. Reaction between 10 g diethylphosphorous acid and 5.5 g ethyl phenylpropiolate gave 7 g ethyl ester of α, β-di-(diethylphosphono)-phenylpropionic acid (Table 3, compound 3).

Found %: P 13.96; 13.88

$C_{19}H_{22}O_5P_2$ Calculated %: P 13.78

Addition of diethylthiophosphorous acid to ethyl phenylpropiolate. Reaction between 10.8 g diethlthiophosphonous acid and 6.1 g ethyl phenylpropiolate was performed in presence of sodium ethylate. Fractionation of the reaction mixture gave 2.5 g ethyl ester of -(diethylthiophosphono)-cinnamic acid (Table 3, compound 4) and 2.4 g ethyl ester of α, β-di-(diethylthiophosphono)-phenylpropionic acid (Table 3, compound 5). The latter is a very viscous liquid.

Analysis of compound 4

Found %: P 9.75; 9.68

$C_{15}H_{21}O_4PS$. Calculated %: P 9.45

Analysis of compound 5

Found %: P 12.66; 12.87

$C_{19}H_{32}O_6P_2S_2$. Calculated %: P 12.86

Addition of ethyl ester of ethylphosphorous acid to ethyl phenylpropiolate. Reaction of 4.2 g ethyl ester of ethylphosphorous acid with 3 g ethyl phenylpropiolate gave 1.5 g addition product (Table 3, compound 6).

Found %: P 10.57

$C_{19}H_{22}O_6P_2$. Calculated %: P 10.45

Addition of diethylthiophosphorous acid to diethyl acetylenedicarboxylate. Reaction was effected between 7.2 g diethylthiophosphorous acid and 4 g diethyl acetylenedicarboxylate. There was obtained 2.3 g diethyl ester of α,β-di-(diethylthiophosphono)-succinic acid (Table 3, compound 7).

Found %: P 13.25; 13.00

$C_{16}H_{32}O_8P_2S_2$. Calculated %: P 12.97

SUMMARY

1. Addition of diethylthiophosphorous acid to esters of acrylic, methacrylic, cinnamic and maleic acids gave high yields of esters of dialkylthiophosphonopropionic, dialkylthiophosphonoisobutyric, dialkylthiophosphonophenylpropionic and dialkylthiophosphonosuccinic acids.

2. Addition was effected of esters of ethyl- and phenylphosphorous acids to esters of crotonic, cinnamic and maleic acids.

3. Addition of dialkylphosphorous acids, of ethylethylphosphonite and of ethyl diethlthiophosphorite to esters of phenylpropiolic and acetylenedicarboxylic acids gave esters of dialkylphosphono- and dialkylthiophosphono- cinnamic acid, esters of di-(dialkylphosphono)- and di-(diethylthiophosphono)- phenylpropionic acid and esters of di-(diethylthiophosphono)-succinic acid.

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[1] See Consultants Bureau Translation, p. p. 537, 1189, 2103.
[2] " " " p. 2035.
[3] " " " p. 921.
[4] " " " p. p. 657; 803.
[5] " " " p. 531.
[6] " " " p. 825.
[7] " " " p. 1415.
[8] " " " p. 537.
[9] " " " p. 831;
[10] " " " p. 661.
[11] " " " p. 825.

MECHANISM OF REACTION OF PHOSPHORUS PENTACHLORIDE WITH CARBOXYLIC ACID AMIDES*

A. V. Kirsanov

In all textbooks, handbooks, and reference books of organic chemistry, it is stated that the action of phosphorus pentachloride on unsubstituted amides of carboxylic acids leads to formation of phosphorus oxychloride and amidochlorides:

$$RCONH_2 + PCl_5 \longrightarrow POCl_3 + RCCl_2NH_2.$$

It is impossible, however, to isolate the amidochlorides in the pure form since they are extremely unstable and break down in the conditions of formation.

$$RCCl_2NH_2 \longrightarrow HCl + RCCl{=}NH,$$

i.e., formation takes place of hydrogen chloride and imidochlorides which likewise decompose and the final products are the nitriles of the carboxylic acids:

$$RCCl{=}NH \longrightarrow HCl + RC{\equiv}N.$$

Such a mechanism of the reaction between phosphorus pentachloride and carboxylic acid amides was proposed as far back as 1858 by Gerhardt [1]; in 1877 it was studied by Wallach [2] and since then it has been unreservedly accepted by all scientists who have investigated the reaction of phosphorus pentachloride with carboxylic acid amides [3].

Wallach encountered several reactions which could not be explained by his scheme and called for additional clarifications, of these the most important are the following: on reacting phosphorus pentachloride with trichloroacetamide, Wallach [2] obtained not the amido chloride but a phosphorus-containing compound whose composition and molecular weight corresponded to the formula C_2Cl_5ONP, and he attributed to it the structure $CCl_3CCl{=}NPOCl_2$. In order to account for the formation of this substance, Wallach proposed a supplementary scheme according to which the imidochloride formed in this reaction can enter into reaction with phosphorus oxychloride:

$$RCCl{=}NH + POCl_3 \longrightarrow HCl + RCCl{=}NPOCl_2,$$

i.e. with formation of chlorides of imidochloride-N-phosphoric acids. Compounds of a similar type were later prepared by Steinkopf [4] who accepted for them the mechanism of formation and the structure proposed by Wallach.

It must be noted that when discussing the possible structure of the phosphorus-containing compound obtained from trichloroacetamide and phosphorus pentachloride, Wallach considered only two formulas, namely $CCl_3CONClPCl_2$ and $CCl_3CCl{=}NPOCl_2$ and overlooked a third theoretically possible formula $CCl_3CON{=}PCl_3$. It should also be pointed out that the supplementary hypothesis of reaction of the imidochlorides with phosphorus oxychloride was not checked experimentally, has never been confirmed, and obviously originated in the desire to give some sort of explanation of the mechanism of the reaction through intermediate formation of amidochlorides or imidochlorides.

A second fact which did not fit in with Wallach's scheme was the reaction (which he discovered) of the amidochloride prepared from ethyl oxamate with phenols and alcohols [5]. In this reaction in place of the expected iminoesters which should have been formed according to the scheme:

$$C_2H_5COCCl_2NH_2 + HOR \longrightarrow C_2H_5OCOC(OR){=}NHHCl + HCl,$$

there were actually obtained etnyl chloride and esters of oxamic acid with the same alcohol which was introduced into the reaction, i.e. the process took place according to the scheme:

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$$C_2H_5OCOCl_2NH_2 + HOR \rightarrow C_2H_5Cl + HCl + ROCOCONH_2.$$

Wallach did not give any convincing explanation of this mechanism.

In 1909 Titherley and Worrall [6] studied the action of phosphorus pentachloride on benzamide and established that the first product of the reaction is evidently a substance with the composition $C_6H_5CONPCl_2$, but they failed to isolate this compound in the pure state. On exposing a solution of the original product to the action of atmospheric moisture, Titherley and Worrall obtained a nearly quantitative yield of benzoylaminophosphoryl chloride $C_6H_5CONHPOCl_2$ which on heating broke down quantitatively to benzonitrile, hydrogen chloride, phosphorus oxychloride and metaphosphoric acid.

Notwithstanding all these inconsistencies, Wallach's scheme has not been subjected to criticism since its publication in 1877 to the present day and is cited as incontestable fact not only in reference books but even in all elementary textbooks of organic chemistry.

Recently it was found that amides of sulfonic acids easily and quantitatively react with phosphorus pentachloride with evolution of hydrogen chloride and formation of the corresponding trichlorophosphazosulfo compounds according to the scheme:

$$RSO_2NH_2 + PCl_5 \rightarrow 2HCl + RSO_2N{=}PCl_3.$$

The reaction is general in character and proceeds with equal ease for sulfamic acid [7], sulfamide [8], amides of aromatic sulfonic acids [9] and amides of alicyclic sulfonic acids.

The mechanism of reaction of phosphorus pentachloride with amides of sulfuric acid is probably as follows. At the outset the PCl_4^+ ion attaches itself to the coordinatively unsaturated nitrogen atom

$$RSO_2NH_2 + PCl_4^+ \rightarrow RSO_2\underset{\displaystyle PCl_4}{\overset{\displaystyle |}{N}}H_2^+$$

Then the unstable intermediate product is stabilized with splitting-off of hydrogen chloride and a proton:

$$RSO_2\underset{\displaystyle PCl_4}{\overset{\displaystyle |}{N}}H_2^+ \rightarrow HCl + RSO_2N{=}PCl_3 + H^+.$$

The proton reacts with the PCl_6^- ion with formation of hydrogen chloride and PCl_5 which immediately breaks down to ions of PCl_4^+ and PCl_6^-.

Carboxylic acid amides are not strictly analogs of amides of sulfonic acids, but the nitrogen atom of the amides is likewise coordinatively unsaturated and is likewise linked to two atoms of hydrogen, as is the nitrogen atom of sulfonic acid amides. There is therefore good reason to assume that the reaction of phosphorus pentachloride with carboxylic acid amides must proceed according to the same mechanism as for sulfonic acid amides, i.e. with formation of trichlorophosphazoacyls according to the scheme:

$$RCONH_2 + PCl_4^+ \rightarrow RCO\underset{\displaystyle PCl_4}{\overset{\displaystyle |}{N}}H_2^+ \rightarrow H^+ + HCl + RCO{=}NPCl_3.$$

It would undoubtedly be wrong, however, to suggest that the properties of trichlorophosphazosulfonacyls must be similar to the properties of trichlorophosphazosulfo compounds. First, these two classes of compounds must differ in thermal stability. On cleavage, the trichlorophosphazoacyls must form phosphorus oxychloride and stable, thermodynamically "advantageous" nitriles:

$$RCON{=}PCl_3 \rightarrow POCl_3 + RCN.$$

Hence, the thermal cleavage of trichlorophosphazoacyls must proceed with great facility and with good yields.

Thermal cleavage of trichlorophosphazosulfo compounds must yield phosphorus oxychloride and unstable alkyl or aryl sulfans which are evidently thermodynamically not too "advantageous" and which have been hitherto unknown:

$$RSO_2N{=}PCl_3 \rightarrow POCl_3 + RSON.$$

Consequently the thermal cleavage of trichlorophosphazosulfo compounds must proceed with great difficulty and with poor yields, as is confirmed by experimental results [10].

We thus have sufficient and reliable experimental and theoretical evidence to throw doubt upon the correctness of Wallach's mechanism, and we may suggest that the action of phosphorus pentachloride on carboxylic acid amides actually leads not to amidochlorides but to trichlorophosphazoacyls which easily break down to phosphorus oxychloride and nitriles:

$$RCONH_2 + PCl_5 \rightarrow 2HCl + RCON{=}PCl_3 + POCl_3 + RCN$$

Formation of imidochlorides is readily accounted for by the following reaction of HCl with nitriles: RCN + $\rightarrow$RCCl=NH or more probably: $RC{\equiv}NH^+ + Cl^-$. The latter reaction does not call for confirmation since it is the usual method of preparation of imidochlorides [11]. The newly proposed mechanism does not, however, explain the formation of amidochlorides which, according to the generally accepted scheme of Wallach, are the first products of the reaction. A detailed study of Wallach's original papers established that Wallach did not isolate in the pure state a single one of the amidochlorides of the type of $RCCl_2NH_2$ in the reaction of phosphorus pentachloride with carboxylic acid amides. The crude products obtained by Wallach were only analyzed for chlorine, in which connection the analytical data were very different from the calculated theoretical values and frequently were more consistent with the composition of trichlorophosphazoacyls than with the composition of amidochlorides.

In a study of the reaction of acetamide and benzamide with phosphorus pentachloride, Wallach failed to isolate any pure substances, for which reason he wrote: "acetamide is not a suitable model for the study of the reaction of phosphorus pentachloride with carboxylic acid amides". He chose as a model the ethyl ester of oxamic acid. This choice must be considered most unfortunate, for oxalic acid and its amides differ sharply in properties both from the common monobasic carboxylic acids and from all other dibasic carboxylic acids and their amides. It suffices to recall the exceptionally easy oxidizability of oxalic acid and its derivatives, sharply differentiating it from the overwhelming majority of the remaining saturated carboxylic acids, or the characteristic reaction of oxalic acid esters with phosphorus pentachloride. Moreover, we must reckon with the possibility of reaction of phosphorous pentachloride not only with the carbamido group but also with the carbethoxy. Consequently the data obtained for ethyl oxamate cannot be regarded as typical of the behavior of amides of all other carboxylic acids. Moreover, even these data, when examined critically, do not provide any evidence that the first product of reaction of ethyl oxamate with phosphorus pentachloride is the corresponding amidochloride. Wallach reported that one molecule of phosphorus pentachloride acts on ethyl oxamate without evolution of hydrogen chloride, the product being a colorless, transparent liquid which deposits crystals on cooling, but Wallach did not succeed in isolating the crystals in the pure state. In the best case the chlorine content of this substance was 4.12% less than required for the amidochloride. Other analyses were not performed. No characteristic reactions demonstrating that the substance really was an amidochloride were carried out, if we except the thermal cleavage of the crude reaction product which led to a low yield of cyanoformic ester.

Wallach also gives a detailed description of the formation from the reaction mixture by the action of atmospheric moisture of a pure compound with the composition $C_4H_6O_3Cl_4NP$, discusses the possible structure of the substance and expresses surprise apropos of the fact that the substance is undoubtedly only formed in presence of atmospheric moisture. It is impossible to reconcile the formation of this substance with Wallach's hypothesis of primary formation of an amidochloride with the structure $C_2H_5OCOCCl_2NH_2$, since it is altogether improbable that under the action of atmospheric moisture phosphorus oxychloride could add on to an amidochloride, while in the absence of atmospheric moisture the substance is not formed. Wallach did not put forward any explanation of the formation of the compound $C_4H_6O_3Cl_4NP$ but nevertheless considered that the formation of amidochlorides by the action of phosphorus pentachloride on carboxylic acid amides had been completely demonstrated. Thus a close examination of Wallach's paper shows that the formation of an amidochloride during the action of phosphorus pentachloride on ethyl oxamate was not only not proved but was even extremely improbable.

The reaction of phosphorus pentachloride with carboxylic acid amides was studied not only by Wallach but also by a number of other workers [3, 4, 6]. None of them succeeded in isolating amidochlorides and none of them demonstrated their formation by the action of phosphorus pentachloride on unsubstituted carboxylic acid amides by any trustworthy indirect methods. Consequently there are no reliable experimental data to prove that amidochlorides are obtained by the action of phosphorus pentachloride on carboxylic acid amides. It was only due to the great reputation of Wallach as a scientist that his unfounded and erroneous conclusions about the reaction of phosphorus pentachloride with carboxylic acid amides were accepted quite uncritically and have been regarded as entirely true for over 75 years.

For a final solution of the problem it was necessary to make an experimental study of the reaction of phosphorus pentachloride with carboxylic acid amides and to check and clarify the conflicting and confused results of Wallach regarding the reaction of phosphorus pentachloride with ethyl oxamate.

The first substance selected as a model was benzamide, since the data obtained with benzamide can be applied with minor reservations to amides of other carboxylic acids. It was found that phosphorus pentachloride readily reacts with benzamide. On conducting the reaction between equivalent amounts of reactants in carbon tetrachloride solution at 70°, the process is completed in the course of a few minutes and about 90% of the hydrogen chloride is evolved according to the equation:

$$C_6H_5CONH_2 + PCl_5 \rightarrow 2HCl + C_6H_5CON{=}PCl_3$$

After the solvent had been driven off in vacuum at 70°, there remained a colorless transparent liquid which rapidly crystallized completely. The amount of crude product corresponded to 97.7% of that according to the above equation. The melting point of the crude product was 58° (thermometer bulb in the liquid, disappearance of the last crystal). The substance crystallizes from ligroine of boiling range 85-95°. The yield of completely pure product is 78.0% of the theoretical; m. p. 60-61°. The composition and molecular weight of the substance correspond to the formula $C_6H_5CONPCl_3$. The product readily reacts with water, alcohols and phenols. On heating, it breaks down quantitatively to phosphorus oxychloride and benzonitrile. By the action of atmospheric moisture in benzene solution, or better by the action of 1 mole anhydrous formic acid in benzene solution, it is converted in nearly quantitative yield into the chloride of benzoylamidophosphoric acid which was previously obtained by Titherley.

Consequently there is no doubt whatever that the substance in question is trichlorophosphazobenzoyl $C_6H_5CON{=}PC$ or a product of its isomerization – the chloride of the N-phosphoric acid of benzimidochloride $C_6H_5CCl{=}NPOCl_2$. An isomerization of this type is not excluded since phosphorus possesses a great affinity for oxygen. The nearly theoretical yield of crude product, the closeness of the melting points of the crude and pure substances, the high yield of hydrogen chloride and the absence from the distillate of appreciable amounts of phosphorus oxychloride completely exclude Wallach's mechanism for the reaction of benzamide with phosphorus pentachloride and fully confirm the strict accuracy of our new scheme advanced above.

The question naturally arises as to why Wallach and, later, Titherley and Worrall did not obtain trichlorophosphazobenzoyl. The reason is a very simple one. Trichlorophosphazobenzoyl is obtained in nearly quantitative yield only when the mixture of phosphorus pentachloride, benzamide and carbon tetrachloride is, shortly after mixing, at once raised to at least 50-60° and after the conclusion of the reaction the solvent is immediately driven off completely in a good vacuum. If the mixture is allowed to stand at room temperature before heating or if the reaction is performed at 30° or the mixture is allowed to stand after carrying out the reaction, then the yields of trichlorophosphazobenzoyl fall sharply and its isolation becomes impossible in practice. Wallach entirely failed to detect this phenomenon. Titherley and Worrall did indeed detect it but could not find its explanation.

The explanation proved to be very simple. Hydrogen chloride has a remarkably strong catalytic effect upon the cleavage of trichlorophosphazobenzoyl into phosphorus oxychloride and benzonitrile. In the absence of hydrogen chloride the reaction proceeds rapidly and quantitatively only at above 100°. At room temperature, certainly in the absence of moisture, trichlorophosphazobenzoyl can be stored for at least several months without appreciable decomposition although a weak odor of benzonitrile is developed after only a few hours. In presence of hydrogen chloride, for example in solution in carbon tetrachloride saturated with hydrogen chloride, cleavage takes place very quickly and is nearly complete in the course of 20-30 hours at room temperature. It is interesting that phosphorus pentachloride has no catalytic action at all and in its presence (5%) no change occurs in trichlorphosphazobenzoyl in carbon tetrachloride solution at room temperature in the course of three days. Consequently, a condition for obtaining good yields of trichlorophosphazobenzoyl is to perform the reaction and isolate the products in conditions ensuring maximum speed and completeness of removal of hydrogen chloride.

It remains to clear up the problem of the structure of trichlorophosphazobenzoyl, i.e. whether or not it isomerizes in the process of formation into the chloride of the N-phosphoric acid of benzimidochloride:

$$C_6H_5CON{=}PCl_3 \; ?\rightarrow ?\; C_6H_5CCl{=}NPOCl_2$$

A completely rigorous proof of the structure of the product of reaction of phosphorus pentachloride with benzamide can only be obtained with the help of physical methods of investigation; this will be done later. At the present time the structure of trichlorophosphazobenzoyl can be demonstrated by a chemical method.

Reaction of trichlorophosphazobenzoyl with dry sodium phenate in benzene solution at a temperature not higher than 80° gives a nearly quantitative yield of the well-crystallized triphenyl ester of benzoylimidophosphoric acid (triphenoxyphosphazobenzoyl):

$$C_6H_5CON{=}PCl_3 + 3C_6H_5ONa \rightarrow 3NaCl + C_6H_5CON{=}P(OC_6H_5)_3.$$

When distilled or when kept at room temperature for a week in presence of traces of hydrogen chloride, the triphenyl ester of benzoylimidophosphoric acid quantitatively breaks down to benzonitrile and triphenyl phosphate according

to the scheme:

$$C_6H_5CON{=}P(OC_6H_5)_3 \rightarrow C_6H_5CN + OP(OC_6H_5)_3.$$

This cleavage proves that the triphenyl ester of benzoylimidophosphoric acid and consequently also trichlorophosphazobenzoyl are indeed phosphazo compounds and not their isomers with a phenoxy group and chlorine atom at the carbon atom:

$$C_6H_5C(OC_6H_5){=}NPO(OC_6H_5)_2 \quad \text{and} \quad C_6H_5C(Cl){=}NPOCl_2,$$

since it is extremely improbable that one would obtain from $C_6H_5CCl{=}NPOCl_2$ and $3C_6H_5ONa$ at 80° the triphenyl ester of benzoylimidophosphoric acid, and also extremely improbable that in such mild conditions the phenoxy group would migrate from the carbon to the pentavalent phosphorus. Migration of an oxygen atom from carbon to phosphorus is quite often observed. Consequently we can claim that proof has been obtained, as far as this is possible by a purely chemical method, that the first product of the reaction of phosphorus pentachloride with benzamide is trichlorophosphazobenzoyl.

Wallach [2] also obtained from the amides of dichloro- and trichloroacetic acids compounds with the composition $RCONPCl_3$ to which he assigned, without any proof, the structure $RCCl{=}NPOCl_2$. Wallach explained the formation of these compounds, once again without any experimental basis, by the scheme:

$$RCONH_2 + PCl_5 \rightarrow RCCl_2NH_2 + POCl_3;$$
$$RCCl_2NH_2 \rightarrow HCl + RCCl{=}NH + HCl;$$
$$RCCl{=}NH + POCl_3 \rightarrow HCl + RCCl{=}NPOCl_2.$$

Later Steinkopf [4] obtained several analogous compounds from amides of a series of substituted acetic acids and accepted for them the structure and formation mechanism proposed by Wallach.

If Wallach's scheme were correct, then the final phosphorus compounds should have been obtained not only from phosphorus pentachloride and amides of carboxylic acids but also from imidochlorides and phosphorus oxychloride. Neither Wallach nor Steinkopf carried out such experiments. Final refutation of Wallach's scheme was obtained by numerous experiments in the most diverse conditions involving reaction of imidochlorides with phosphorus oxychloride and of nitriles with phosphorus oxychloride and hydrogen chloride. In not a single case was a trichlorophosphoacyl obtained. Consequently Wallach's scheme for the formation of phosphorus-containing products of reaction of phosphorus pentachloride with carboxylic acid amides is entirely erroneous and all the compounds of this type obtained for the reaction of benzamide with phosphorus pentachloride have been confirmed with amides of several substituted benzoic acids.

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The next model substance selected for study of the reaction of phosphorus pentachloride with carboxylic acid amides was ethyl carbamate. If the reaction with ethyl carbamate proceeded according to Wallach's scheme, then the reaction products should be the corresponding amidochloride, imidochloride, ethyl cyanate and ethyl cyanurate. If the reaction proceeded with detachment of ethyl chloride, then the resultant cyanic and (later) cyanuric acid should be obtained according to the equations:

$$NH_2COOC_2H_5 \xrightarrow[+\,PCl_5]{} NH_2CCl_2OC_2H_5 \rightarrow NH{=}CClOC_2H_5;$$

$$NH{=}CClOC_2H_5 \rightarrow N{\equiv}COC_2H_5 \rightarrow C_3N_3(OC_2H_5)_3$$
$$NH{=}CClOC_2H_5 \rightarrow N{\equiv}COH \rightarrow C_3H_3(OH)_3$$

Not one of these products is actually formed. In fact the reaction proceeds according to the general scheme with nearly quantitative formation of the ethyl ester of trichlorophosphazocarbonic acid: -

$$C_2H_5OCONH_2 + PCl_5 \rightarrow 2HCl + C_2H_5OCON{=}PCl_3.$$

This ester is a liquid with a pungent odor, stable at low temperatures. At 45° the ester nearly quantitatively breaks down to ethyl chloride and isocyanophosphoryl chloride according to the equation:

$$C_6H_5OCON{=}PCl_3 \rightarrow C_2H_5Cl + O{=}C{=}NPOCl_2.$$

If heating is not done carefully, the reaction takes place explosively. Isocyanophosphoryl chloride is a colorless liquid, b.p. 136-138°, with a very unpleasant odor recalling the odor of perspiration. Isocyanophosphoryl chloride is very reactive; with alcohols it gives in succession urethanphosphoryl chloride and esters of urethanphosphoric acids:

$$Cl_2PONCO + ROH \rightarrow Cl_2PONHCOOR;$$
$$Cl_2PONHCOOR + 2R'ONa \rightarrow (R'O)_2PONHCOOR,$$

with ammonia and amines it gives the corresponding derivatives of urea, etc. Consequently isocyanophosphoryl chloride may serve as a starting substance for the preparation of the most diverse derivatives of phosphoric acid.

Reaction of phosphorus pentachloride with urea led to the analog of bis-trichlorophosphazosulfone [8], namely bis-trichlorophosphazocarbonyl, m.p. 40-41°:

$$H_2NCONH_2 + 2PCl_5 \rightarrow 4HCl + Cl_3P{=}NCON{=}PCl_3$$

and high-melting products of approximately the same elementary composition which have not yet been investigated.

A study of the reaction of phosphorus pentachloride with ethyl oxamate, which had been the sole experimental basis for Wallach's theory and appeared to confirm the correctness of his proposed mechanism, likewise showed that Wallach's scheme was wrong. It was found that ethyl oxamate readily enters into reaction not only with one but also with two molecules of phosphorus pentachloride, a fact which Wallach failed to notice. The first product of the reaction is not the amidochloride but its isomer with the structure $C_2H_5OCCl_2CONH_2$ i.e. the amide of dichloroethoxyacetic acid, which is formed in a yield of about 60% according to the equation:

$$C_2H_5OCOCONH_2 + PCl_5 \rightarrow C_2H_5OCCl_2CONH_2 + POCl_3,$$

i.e. completely analogous to the esters of dichloroalkoxyacetic acids which are easily formed from esters of oxalic acid [12]:

$$C_2H_5OCOCOOC_2H_5 + PCl_5 \rightarrow C_2H_5OCCl_2COOC_2H_5 + POCl_3.$$

In the case of ethyl oxamate this reaction proceeds with even greater facility than with esters of oxalic acid.

Dichloroethoxy acetamide is a colorless, very easily crystallizing substance, completely stable at temperatures below 100° and melting at 81-82°. The amide is rather slowly decomposed by water and very closely resembles the esters of dichloroalkoxyacetic acids in all its properties. The structure of the compound is fairly rigorously proved by its great stability at room temperature as well as by the formation with alcohols, even though in low yields, of the corresponding esters of oxamic acid and not of iminoesters, according to the scheme:

$$NH_2COCCl_2OC_2H_5 + ROH \rightarrow NH_2COCOOR + C_2H_5Cl + HCl;$$
$$C_2H_5OCOCCl_2NH_2 + ROH ? \rightarrow ? C_2H_5OCOC(OR){=}NHHCl + HCl$$

also by the fact that with alkoxides it gives good yields of amides of the half orthoesters of oxalic acid (amides of trialkoxyacetic acids), according to the reaction:

$$NH_2COCCl_2OR + 2R'ONa \rightarrow 2NaCl + NH_2COC(OR')_2(OR).$$

One compound of this type described in the literature is the amide of the half orthomethyl ester of oxalic acid, obtained from the methyl ester of trimethoxyacetic acid and ammonia [13]. The product obtained from the amide of dichloromethoxyacetic ester and sodium methoxide

$$NH_2COCCl_2OCH_3 + 2CH_3ONa \rightarrow 2NaCl + NH_2COC(OCH_3)_3$$

proved to be identical with the compound described in the literature.

The preparation in good yields of amides of dichloroalkoxyacetic acids simply and naturally explains why Wallach obtained esters of oxamic acid from "amidochlorides" of ethyl oxamate and alcohols (see above). The simple explanation is that the "amidochloride" of Wallach did not contain any amidochloride but contained the amide of dichloroethoxyacetic acid.

The second product of reaction of phosphorus pentachloride with ethyl oxamate is trichlorophosphazo-dichloroethoxyacetyl, formed almost quantitatively according to the equation:

$$C_2H_5OCOCONH_2 + 2PCl_5 \rightarrow C_2H_5OCCl_2CON{=}PCl_3 + 2HCl + POCl_3$$

The same product may be obtained from dichloroethoxyacetamide and one molecule of phosphorus pentachloride. Trichlorophosphazo-dichloroethoxyacetyl is a colorless crystalline compound with m.p. 71-72°, perfectly stable at room temperature; its structure is proved by the method of preparation, by the almost theoretical yields of all the products of the reaction, by the elementary composition, by the molecular weight and by its chemical properties.

Under the action of water vapor in benzene solution, or better by the action of one molecule of anhydrous formic acid, trichlorophosphazodichloroethoxyacetyl is converted in nearly quantitative yield into dichloroethoxy-

acetylamidophosphoryl chloride:

$$C_2H_5OCCl_2CON{=}PCl_3 + HCOOH \rightarrow HCl + CO + C_2H_5OCCl_2CONHPOCl_2.$$

The composition and properties of this substance correspond to the very same product that Wallach isolated from the product of reaction of phosphorus pentachloride with ethyl oxamate after exposure to atmospheric moisture. Consequently, the formation of this substance cannot be reconciled at all with a reaction of an imidochloride with phosphorus oxychloride under the influence of atmospheric moisture, as Wallach had thought, nor with the fact that the trichlorophosphazodichloroethoxyacetyl present in the reaction mixture was hydrolyzed at the first step and gave the considerably more stable dichloroethoxyacetylamidophosphoryl chloride which Wallach was able to isolate in the pure form and to analyze. Trichlorophosphazodichloroethoxyacetyl reacts readily with water, alcohols, phenols, ammonia and amines, just like other trichlorophosphazo compounds. Hence the reaction of ethyl oxamate with phosphorus pentachloride proceeds according to the general scheme but is accompanied by a reaction similar to that of phosphorus pentachloride with esters of oxalic acid.

A close examination of the experimental part of Wallach's paper reveals why he failed to isolate even a single product of the direct interaction of phosphorus pentachloride with ethyl oxamate in the pure form. First, as indicated above, Wallach did not observe that ethyl oxamate readily reacts not only with one molecule but also with two molecules of phosphorus pentachloride. This oversight prevented him from deliberately selecting the most suitable conditions for the formation of one or the other substance and resulted in the reaction product always being a difficultly resolvable mixture. Second, the paper teems with fundamental experimental errors, of which the most important were the following: Wallach "dried" and stored all his substances in desiccators over soda lime or calcium chloride, which was most unwise because the vapor tension of water over these agents is fairly considerable at room temperature, while the vapor tension of water vapor over the products of reaction of ethyl oxamate with phosphorus pentachloride is substantially zero. In other words, Wallach dried the soda lime and calcium chloride with the substances which he had prepared; the latter naturally then hydrolyzed with evolution of hydrogen chloride which reacted with soda lime to produce more water; the latter again reacted with the substances; and so on. The next fundamental error was the lack of quantitative check of the reactions in progress by quantitative determination of the evolved hydrogen chloride and phosphorus oxychloride, which could have been easily effected. Thus, for example, calculation of the amount of hydrogen chloride permits an assessment of the extent to which the reaction proceeds with formation of trichlorophosphazo compound, and calculation of the amount of phosphorus oxychloride permits an assessment of the extent of replacement of oxygen by two atoms of chlorine. These and other experimental defects resulted in Wallach's failure to isolate in the pure form the products of a reaction which proceeds substantially quantitavely; this circumstance retarded for many years the development of this branch of the chemistry of the carboxylic acid amides.

The detailed experimental data and a detailed account of the properties of the compounds discussed and of analogous compounds will be submitted in a series of papers.

SUMMARY

1. The scheme of Wallach for the reaction of unsubstituted carboxylic acid amides with phosphorus pentachloride, generally accepted at the present day, is erroneous. Amidochlorides are not formed in the action of phosphorus pentachloride on unsubstituted carboxylic acid amides.

2. The reaction of unsubstituted amides of carboxylic acids with phosphorus pentachloride actually proceeds with formation of trichlorophosphazoacyls and two molecules of hydrogen chloride.

3. When heated or when exposed to the catalytic action of hydrogen chloride at room temperature, trichlorophosphazoacyls break down to phosphorus oxychloride and nitriles.

4. The structure of the produt of reaction of phosphorus pentachloride with benzamide was established as that of trichlorophosphazobenzoyl by a chemical method.

5. Trichlorophosphazoacyls are extremely reactive and can serve as starting substances for the preparation of the most diverse derivatives of phosphoric acid.

6. Reaction of phosphorus pentachloride with ethyl carbamate gives the ethyl ester of trichlorophosphazocarbonic acid which at 45° cleaves to ethyl chloride and isocyanophosphoryl chloride.

7. Reaction of phosphorus pentachloroide with ethyl oxamate gives at first dichloroethoxyacetamide and then trichlorophosphazo-dichloroethoxyacetyl.

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* See Consultants Bureau Translation, page 101.

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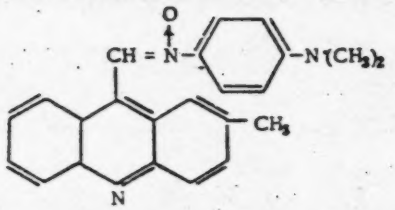
CONDENSATION OF BENZO DERIVATIVES OF 9-METHYLACRIDINE

III. CONDENSATIONS WITH p-NITROSODIMETHYLANILINE

B. M. Mikhailov and G. S. Ter-Sarkisyan

In the previous communications [1,2] it was shown that in passing from 9-methylacridine to its mono- and dibenzo derivatives, the activity of the methyl group is lowered in reactions with aromatic aldehydes and nitroso and diazo compounds. In the present communication we submit the results of an investigation of condensations of 9-methylacridine, 9-methyl-1,2-benzacridine*, 9-methyl-1,2,7,8-dibenzacridine, also of 4-methyl-5,6-benzoquinoline* and 4-methyl-7,8-benzoquinoline, with p-nitrosodimethylaniline in various conditions. The investigation was undertaken with the aim of establishing the activity of the methyl groups of these compounds in dependence on the number and position of the benzene rings in the molecule.

As we know, 9-methylacridine reacts with facility with aromatic nitroso compounds when the starting substances are heated in presence of sodium carbonate or hydroxide, forming the corresponding nitrones and azomethines [3,4,5] whereas α-picoline, quinaldine and lepidine only enter into this reaction in the form of quaternary salts [6]. It was found that 4-methyl-5,6-benzoquinoline, 4-methyl-7,8-benzoquinoline, 9-methyl-1,2-benzacridine and 9-methyl-1,2,7,8-dibenzacridine likewise do not react with p-nitrosodimethylaniline when alcoholic solutions of the components are heated in presence of alkaline catalysts. On the other hand, as our experiments showed, 9-methylacridine condenses with p-nitrosodimethylaniline even at room temperature and in the complete absence of condensing agents. This once again emphasizes the great mobility of the hydrogen atoms of the methyl group of 9-methylacridine in comparison with all the remaining compounds investigated. Also proceeding with ease is the reaction between 2,9-dimethylacridine and p-nitrosodimethylaniline with formation of α-9(2-methylacridyl)-N-(p-dimethylaminophenyl)-nitrone (I):

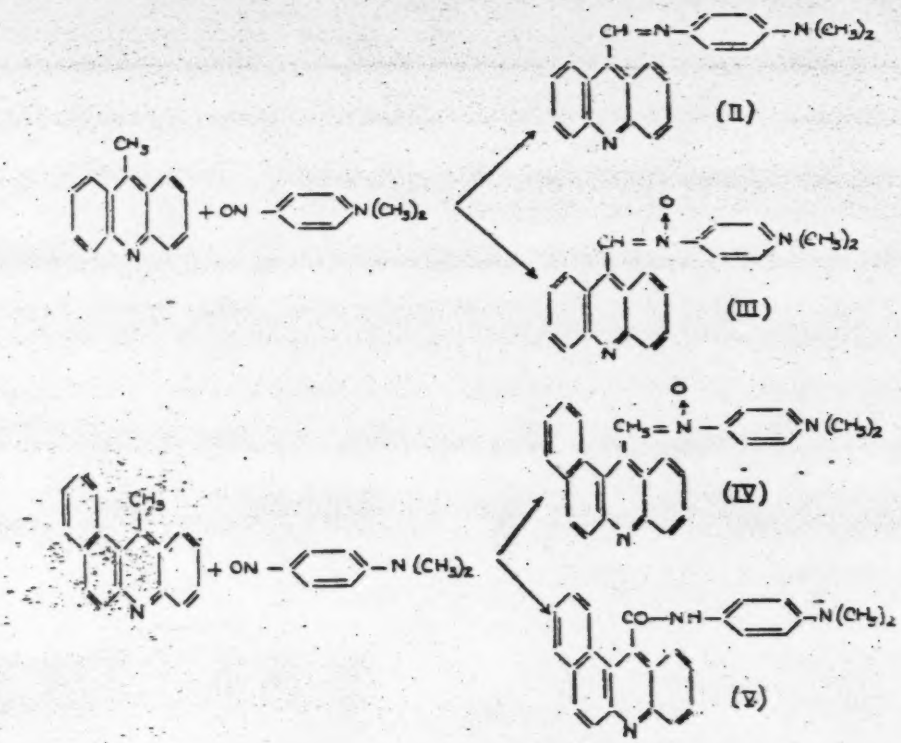


(I)

Study of the photochemical condensations of the above-mentioned compounds with p-nitrosodimethylaniline showed that these reactions could not be effected for 5,6- and 7,8-benzo derivatives of lepidine even under the influence of ultraviolet rays. Only 9-methylacridine and 9-methyl-1,2-benzacridine entered into reaction with p-nitrosodimethylaniline on irradiation of the alcoholic solutions of the starting substances with a PRK-2 quartz mercury lamp; in the first case a mixture of the p-dimethylaminoanil of acridine-9-aldehyde (II) and α-9-acridyl-N-p-dimethylaminophenylnitrone (III) was obtained; in the second case a mixture of α-(1,2-benzacridyl-9)-N-(p-dimethylaminophenyl)-nitrone (IV) and the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid (V): (See page 560).

It is possible that the anilide (V) is obtained by isomerization of the nitrone (IV) under the action of ultraviolet rays. A similar isomerization of α-N-9-acridylphenylnitrone into the anilide of acridine-9-carboxylic acid under the action of sunlight was previously observed by Chardonnens [5].

* Publisher's note. The Russian convention for numbering of benzacridines, etc. differs from that adopted by Chemical Abstracts.



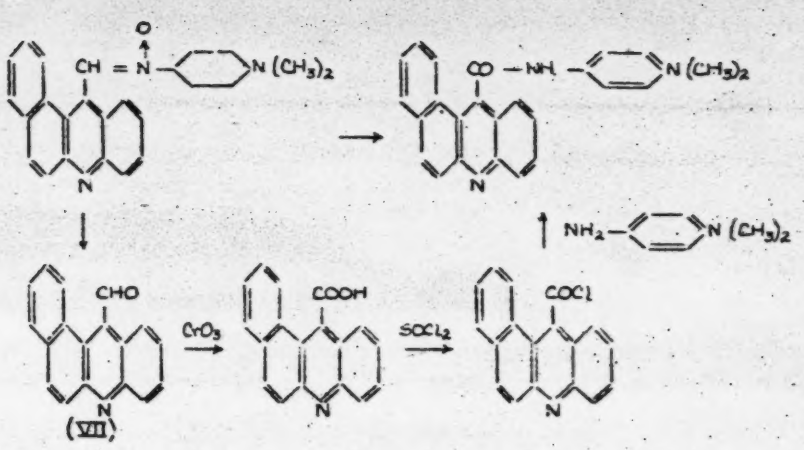
We also observed the formation of the nitrone (IV), the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid (V) and the p-dimethylaminoanil of 1,2-benzacridine-9-aldehyde (VI) in the condensation of 9-methyl-1,2-benzacridine with p-nitrosodimethylaniline hydrochloride. It should be noted that, depending upon the ratios of starting materials and the duration of the experiment, either the anilide (V) or the nitrone (IV) will preponderate in the reaction products; with increasing amount of p-nitrosodimethylaniline hydrochloride the yield of nitrone falls and that of the anilide rises.

It is known that nitrones of the aromatic series are transformed into the anilides of the corresponding acids under the influence of acetic anhydride, acetyl chloride, alcoholic sodium carbonate, etc. [7,8,9]. On the basis of results that we obtained in a study of the condensation of 9-methyl-1,2-benzacridine with p-nitrosodimethylaniline hydrochloride, we suggested that the anilide (V) is a product of isomerization of the nitrone (IV) under the action of the hydrochlorides of the initial or intermediate products of the reaction.

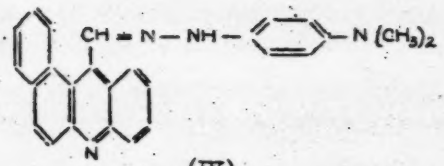
Special experiments on the isomerization of α-1,2-benzacridine-9-N-(p-dimethylaminophenyl)-nitrone (IV) under the influence of amine salts (hydrochlorides of p-nitrosodimethylaniline and aniline) confirmed this suggestion. In all cases the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid was isolated. The structure of the latter was confirmed by synthesis from p-dimethylaminoaniline and 1,2-benzacridine-9-carboxylic acid chloride. This acid, in turn, was obtained by oxidation of 1,2-benzacridine-9-aldehyde (VII), which is formed by hydrolysis of the nitrone (IV) with weak hydrochloric acid. The following series of transformations was thus realized: (See A, page 561).

It may be noted that hydrolysis of the nitrone (I) gave 2-methylacridine-9-aldehyde (VIII).

9-Methyl-1,2-benzacridine, like 9-methyl-3,4-benzacridine [5], couples with p-nitrodiazobenzene, but unlike 9-methylacridine it does not react with diazobenzene, whereas 9-methyl-1,2,7,8-dibenzacridine does not react with either of these diazo compounds. The reaction between 9-methyl-1,2-benzacridine and p-nitrophenyldiazonium proceeds in a medium of glacial acetic acid with formation of compound (IX) which has the structure of the p-nitrophenylhydrazone of 1,2-benzacridine-9-aldehyde: (see B, page 561).



(A)



(B)

(IX)

EXPERIMENTAL

Condensation of 9-methylacridine with p-nitrosodimethylaniline

a) Under the action of ultraviolet rays. A methanol solution of 3 g (0.015 mole) 9-methylacridine and 2.31 g (0.015 mole) p-nitrosodimethylaniline was irradiated in a molybdenum glass flask with a PRK-2 lamp. After 21 hours' irradiation, 2.78 g brown crystalline precipitate with m.p. 233-243° was obtained. Irradiation for a further 50 hours gave a further 1.01 g product with the same m.p. Crystallization from chlorobenzene gave 1.61 g (44.7% of the theoretical) of α-9-acridyl-N-(p-dimethyl-aminophenyl)-nitrone (III) with m.p. 234-235.5° (with decomposition).

Found %: C 77.39; H 5.73.

$C_{22}H_{19}N_3O$. Calculated %: C 77.39; H 5.61.

and 0.7 g (yield 14% of the theoretical) of dark violet crystals of the p-dimethylaminoanil of 9-acridinealdehyde (II) with m.p. 248-249° Chardonnens gives m.p. 243° for the nitrone (III) and m.p. 248° for the azomethine (II).

b) In the dark at room temperature. A methanol solution of 2 g 9-methylacridine and 1.59 g p-nitrosodimethylaniline was left in the dark at room temperature. After 21 days 2.54 g of a mixture of substances was obtained (71% of the amount of starting materials), and after crystallization from chlorobenzene gave 1.14 g of nitrone (III) with m.p. 235.5° (with decomp.) and 0.39 g azomethine (II) with m.p. 248-249°.

α-(2-Methyl-9-acridyl)-N-(p-dimethylaminophenyl)-nitrone (I)

0.5 g (0.0024 mole) 2,9-dimethylacridine and 0.36 g (0.0024 mole) p-nitrosodimethylaniline were dissolved in 10 ml methanol. To the solution was added 3 drops conc. sodium carbonate solution and the mixture heated under a reflux condenser for 5 hours. After cooling, 0.22 g dark-cherry precipitate with m.p. 215-220° was filtered from the solution. After crystallization from dioxane, xylene and ethyl acetate, α-(2-methyl-9-acridyl)-N-(p-dimethylaminophenyl)-nitrone formed lustrous, dark-red crystals with m.p. 224-225°.

Found %: C 77.49; H 5.85; N 12.11

$C_{23}H_{21}N_3O$. Calculated %: C 77.72; H 5.95; N 11.82

2-Methylacridine-9-aldehyde (VIII)

0.22 g α-(2-methyl-9-acridyl)-N-(p-dimethylaminophenyl)-nitrone was dissolved in 10 ml 5% hydrochloric acid at room temperature. A yellow precipitate of 2-methylacridine-9-aldehyde hydrochloride rapidly came down. It was filtered, shaken with water and neutralized with a few drops of ammonia. Yield 0.11 g with m.p.

about 130°. After crystallization from ligroine, 2-methylacridine-9-aldehyde formed yellow crystals with m.p. 136-138°. Readily soluble in the common organic solvents.

Found %. N 6.61
$C_{15}H_{11}NO$. Calculated %. N 6.33

Photocondensation of 9-methyl-1,2-benzacridine with p-nitrosodimethylaniline

A methanol solution of 2 g (0.008 mole) 9-methyl-1,2-benzacridine and 1.24 g (0.008 mole) p-nitrosodimethylaniline was irradiated with a PRK-2 lamp in a nitrogen atmosphere for 200 hours. The color of the solution gradually changed to dark-brown and a yellow-brown deposit appeared at the bottom of the flask. After the completion of irradiation, 0.42 g yellow-brown precipitate was filtered off; m.p. 201-212° (with decomp.). Crystallization of the reaction product from benzene gave 0.05 g yellow substance with m.p. about 300° and 0.15 g yellow-orange crystalline precipitate with m.p. 223° (with decomp.). After three recrystallizations of the latter substance from chlorobenzene, α-9-(1,2-benzacridyl)-N-(p-dimethylaminophenyl)-nitrone (IV) was obtained in the form of bright-yellow, long needles with m.p. 229-230° (with decomp.). The nitrone is sparingly soluble in ethyl alcohol and benzene, readily soluble in hot chlorobenzene. The nitrone crystallizes from ethyl alcohol in two isomorphic forms — small, bright-yellow needles and orange platelets. Both types of crystals have the same melting point and elementary composition.

Found %. C 79.71; H 5.64; N 10.67
$C_{26}H_{21}N_3O$. Calculated %. C 79.75; H 5.41; N 10.73

Evaporation of the primary alcoholic mother liquor to half its volume led to separation of the substance with m.p. approx. 300°; after two crystallizations from chlorobenzene, this was in the form of fine, yellow needles with m.p. 290-291° (with decomp.); its analysis corresponded to the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid

Found %. C 80.14; H 5.72
$C_{26}H_{21}N_3O$. Calculated %. C 79.75; H 5.41

A mixture with a synthetic specimen of the same anilide did not give a depression of m.p.

Condensation of 9-methyl-1,2-benzacridine with p-nitrosodimethylaniline hydrochloride.

a) Into a hot ethanol solution of 1 g (0.004 mole) 9-methyl-1,2-benzacridine was introduced 0.6 g (0.0032 mole) p-nitrosodimethylaniline hydrochloride; the mixture was then heated for 15 minutes. At the end of the heating the solution deposited long yellow needles which were filtered, washed with ethyl alcohol and dried (0.51 g, m.p. 216-220° with decomp.). After two crystallizations from chlorobenzene the substance had m.p. 225-227° (with decomp.) and was α-9-(1,2-benzacridyl)-N-(p-dimethylaminophenyl)-nitrone (IV). A mixed sample with the nitrone obtained by photocondensation did not give a depression of m.p. On diluting the original mother liquor with water and crystallizing the resultant precipitate from ethyl alcohol, 0.08 g p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid was obtained, m.p. 277-280° (with decomp.). The following were also obtained from the liquor: 0.12 g nitrone with m.p. 210-216° and 0.27 g of the original 9-methyl-1,2-benzacridine with m.p. 140-144°.

b) In an experiment with the same ratio of components and 3 hours' heating, 1.2 g 9-methyl-1,2-benzacridine yielded 0.4 g p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid with m.p. 288-290° (with decomp.). On dilution of the primary mother liquor and recrystallization of the resultant precipitate from ethyl alcohol, a further 0.5 g p-dimethylaminobenzanilide of 1,2-benzacridine-9-carboxylic acid, m.p. 267-275° (with decomp.) was obtained, together with 0.16 g of a substance with m.p. 159-164° which after two recrystallizations from the same solvent was isolated in the form of yellow-orange needles with m.p. 168-169° and whose analysis corresponded to that of the p-dimethylaminoanil of 1,2-benzacridine-9-aldehyde (VI)

Found %. C 83.30; H 5.78
$C_{26}H_{21}N_3$. Calculated %. C 83.17; H 5.64

The azomethine (VI) is more soluble in ethyl alcohol and benzene than is its corresponding nitrone (IV). Gentle heating of a solution of the azomethine with dilute hydrochloric acid in presence of phenylhydrazine hydrochloride leads to a copious violet precipitate of the phenylhydrazone of 1,2-benzacridyl-9-aldehyde.

c) As a result of doubling the amount of p-nitrosodimethylaniline hydrochloride and a 15 minutes' duration of the experiment, from 0.5 g 9-methyl-1,2-benzacridine and 0.6 g p-nitrosodimethylaniline hydrochloride was obtained 0.43 g crystalline precipitate with m.p. 262-275° (with decomp.); this was recrystallized from glacial acetic acid and then from chlorobenzene, giving the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid with m.p. 288-290° (with decomp.) (mixed test).

Isomerization of α-9-(1,2-benzacridyl)-N-(p-dimethylaminophenyl)-nitrone into the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid

0.1 g nitrone (IV) with m.p. 225-227° (with decomp.) was heated in 10 ml ethyl alcohol in presence of 0.1 g 9-methyl-1,2-benzacridine hydrochloride for 3 hours. After cooling to room temperature, 0.04 g dark-yellow, fine crystals with m.p. 272-282° (with decomp.) was filtered off. After crystallization from chlorobenzene the m.p. was 282-286° (with decomp.), and no depression was obtained in admixture with a synthetic specimen of the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid. The same results were obtained when using the hydrochlorides of p-nitrosodimethylaniline and aniline as catalysts.

1,2-Benzacridine-9-aldehyde (VII).

0.1 g α-9-(1,2-benzacridine)-N-(p-dimethylaminophenyl)-nitrone was dissolved in 2 ml 10% hydrochloric acid. The transparent solution was heated on a water bath for 15 minutes. Small yellow needles came down and were filtered off, suspended in 7 ml water and neutralized by heating in 1 ml of 2 N sodium acetate solution. The product of reaction was filtered from the warm solution and dried. Yield 0.05 g with m.p. 176-180° (76% of the theoretical). Crystallization from benzene gave bright yellow needles with m.p. 183-184°, the analytical data for which agreed with the composition of 1,2-benzacridine-9-aldehyde

	Found %	C 84.02; H 4.35
$C_{18}H_{11}NO$.	Calculated %	C 84.03; H 4.31

1,2-Benzacridine-9-carboxylic acid

To a warm solution of 0.18 g 1,2-benzacridine-9-aldehyde in 5 ml glacial acetic acid was gradually added an acetic acid solution of 0.07 g chromic oxide and the mixture was heated on a water bath for 1.5 hours. The warm reaction mass was poured into water, the resultant precipitate was filtered off, treated with dilute ammonia and again filtered. The alkaline filtrate was acidified with hydrochloric acid until acid to Congo. The separated 1,2-benzacridine-9-carboxylic acid formed yellow crystals with m.p. 267-270° (with decomp.). Yield 0.066 g or 31.4% of the theoretical. The literature gives m.p. 276° (with decomp.) [10].

p-Dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid

A mixture of 0.13 g 1,2-benzacridine-9-carboxylic acid and 2.6 ml thionyl chloride was heated until the acid had completely dissolved. After driving off the excess of thionyl chloride, the yellow precipitate was heated on a water bath with 0.4 g freshly prepared p-dimethylaminoaniline for ½ hour and then treated with water containing a little ammonia. The obtained precipitate (0.13 g) crystallized from chlorobenzene in the form of fine yellow needles of the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid with m.p. 288-290° (with decomp.). The compound is poorly soluble in common organic solvents and differs from the nitrone (IV) in not being hydrolyzed by weak acids with formation of 1,2-benzacridine-9-aldehyde.

Coupling of 9-methyl-1,2-benzacridine with p-nitrodiazobenzene

0.5 g (0.002 mole) 9-methyl-1,2-benzacridine was dissolved in 15 ml glacial acetic acid. To the solution was added 1.5 g sodium acetate followed, with constant stirring, by 1.5 ml aqueous solution of p-nitrodiazobenzene (prepared by the usual method). On addition of the first few drops of diazo compound the color of the solution changed from light-yellow to cherry red and a dark, amorphous precipitate then came down. The following day 0.66 g of the dark-cherry salt of the dye was filtered off. The base was obtained by heating the salt with dilute ammonia. Yield 0.46 g in the form of yellow-orange crystals with m.p. approx. 300° (yield 57.5% of theoretical).

After many recrystallizations from xylene and then from benzene polychlorides, the compound formed fine plates with m.p. 262.5-264.5°. The compound is sparingly soluble in common organic solvents, readily soluble in pyridine.

	Found %	C 73.20; H 4.03
$C_{24}H_{16}N_4O_2$	Calculated %	C 73.45; H 4.11

SUMMARY

1. 9-Methylacridine is able to condense with p-nitrosodimethylaniline in the dark, at room temperature and without the presence of any catalysts. This reaction proceeds at a much greater velocity under the influence of ultraviolet rays.

2. 9-Methyl-12-benzacridine condenses with p-nitrosodimethylaniline when irradiated with ultraviolet light and forms α-9-(1,2-benzacridine)-N-(p-dimethylaminophenyl)-nitrone and the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid.

3. Condensation of 9-methyl-1,2-benzacridine with the hydrochloride of p-nitrosodimethylaniline leads to three substances: p-dimethylaminoanil-1,2-benzacridine-9-aldehyde (VI), α-9-(1,2-benzacridyl)-N-(p-dimethylaminophenyl)-nitrone (IV) and the p-dimethylaminoanilide of 1,2-benzacridine-9-carboxylic acid (V). The nitrone (IV) undergoes rearrangement into the anilide (V) under the action of amine salts.

4. 9-Methyl-1,2-benzacridine does not react with diazobenzene but couples with p-nitrodiazobenzene in glacial acetic acid.

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HIGH MOLECULAR COMPOUNDS

64. THE POLYCONDENSATION OF THE ETHYL ESTER OF D,L-ALANINE

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Although α-amino acids are readily available substances, many of their transformations and, in particular their polycondensations, have been very little studied. The literature contains only a few reports of experiments on the heating of the amino acids themselves or of their esters with formation of the corresponding polyamides and diketopiperazines.

Thus Curtius [1] and Fischer [2] gave a number of examples in illustration of the ability of esters of α-amino acids to form both linear polymers and cyclic dimers (diketopiperazines). Frenkel and Katchalski [3], and later Pacsu [4] carried out polycondensations of esters of α-amino acids. Frenkel and Katchalski obtained linear polymers with a polymerization coefficient of 14 to 110.

Polyakova and Vereshchagin [5] observed the influence of pressure on the formation of polypeptide chains. Bresler and Glikina [6] showed that alanine ester in aqueous solution under a pressure of 5000 atm. forms a diketopiperazine, while trialanine ester forms a polymer with a polymerization coefficient of 12-15.

We have studied the polycondensation of the ethyl ester of D,L-alanine in various temperature conditions with special reference to the clarification of the effect of catalysts on this reaction.

We prepared the starting ethyl ester of D,L-alanine by Fischer's method [7] and finally purified it by vacuum distillation in carbon dioxide-free air in the special apparatus described below.

EXPERIMENTAL PROCEDURE

We established that carbon dioxide is an extremely active catalyst for the polycondensation of alanine ester, and this necessitated the preparation of the starting material and the performance of the polycondensation reaction itself in conditions ensuring complete absence of carbon dioxide; it was necessary to have a method of exact proportioning of the minute amounts of carbon dioxide employed as catalyst. The polycondensation reaction was therefore performed in sealed ampoules heated in a thermostat at 55 ± 0.1°. The ampoules were filled in the apparatus sketched in Fig. 1 which permitted preparation of carbon dioxide-free ester and the proportioning of small additions of carbon dioxide and other catalysts.

The apparatus consists of a flask A, equipped with a condenser joined through a ground-glass connection with a chamber B, whose side tubes are joined by ground-glass connections to a round-bottomed flask O and special receivers for weighed amounts of ester; the shape of these receivers varies with the nature of the catalyst. When the catalyst is carbon dioxide the receiver sketched in more detail in Fig. 2 is used, while in the case of other catalysts the simpler receiver illustrated in Fig 3 is used.

When carrying out the polycondensation reaction in presence of carbon dioxide, the gas buret E is first filled with carbon dioxide via the limb F while the tap K is closed and tap L is open. The apparatus is then pumped out with a vacuum pump to a residual pressure of 2-3 mm and again filled with dry carbon dioxide which had been dried over sulfuric acid. The carbon dioxide is derived from chemically pure sodium bicarbonate and sulfuric acid. These operations are repeated six times and dry nitrogen is passed through after filling of the buret with carbon dioxide and closing tap L and limb F. After this the apparatus for proportioning the carbon dioxide is weighed on an analytical balance.

The apparatus set up in this manner (see Fig.2) is joined by ground-glass connection to the bulb C to which is attached the condenser (see Fig. 1). In the distillation flask A is placed 1 to 1.5 g freshly prepared alanine ester which had been dried over dry potassium carbonate; the ester is distilled in vacuum (2-4 mm). The ethyl ester of alanine, coming over at 26-30°, enters the receiver C and is run into ampoule D. After 20-25 drops of the ester had collected in the receiver, the bulb B is switched round and the remaining ester is collected in flask O. While the vacuum pump is running, the receiver C is sealed off from the remainder of the proportioning system. The receiver C is then removed with the bulb B, the ground-glass joint being carefully cleansed from vacuum grease, and weighed on an analytical balance together with the rest of the proportioning apparatus. To the difference between the weights is added the weight of the air in the ampoule, and the result is the weight of the ester (usually 0.2-0.4 g). The branch F is then filled with sulfuric acid, with tap K opened,

through tap K is introduced the required amount of carbon dioxide. Tap K is closed and ampoule D is sealed from the buret E at the point N. A sealed ampoule G is thus obtained which contains a weighed amount of ester and a known amount of carbon dioxide as catalyst. The ampoule is at once placed in the thermostat and heated for the required period.

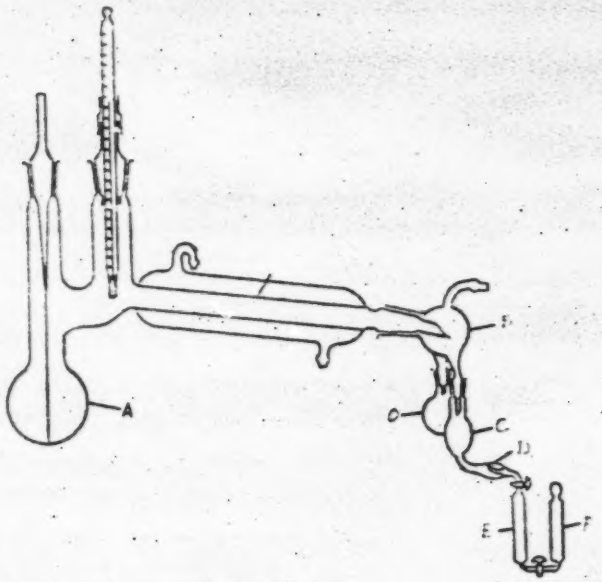

Fig. 1

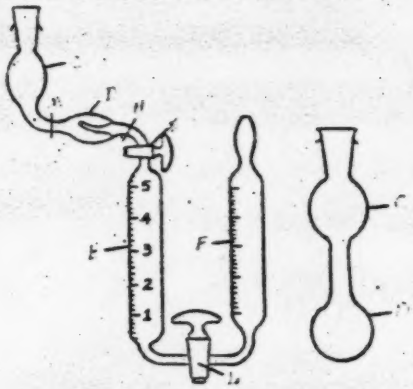

Fig. 2

Fig. 3

In experiments carried out with other catalysts, the fitment shown in Fig. 3 is used, into the latter is previously introduced the required amount of catalyst; then the required amount of ester is distilled into it and the vessel is sealed off under vacuum at point M.

After the heating, the ampoule is withdrawn from the thermostat, rapidly cooled, and crushed in a small, strong porcelain beaker to which is previously added 10-20 ml of 3% aqueous acetic acid. The resultant solution is poured into a measuring flask, the beaker is rinsed out with fresh portions of acetic acid which are also transferred to the flask; the volume is then made up to the mark with additional 3% acetic acid solution. The content of free amino groups in the solution is then determined by the Van Slyke method [8].

A series of experiments in which the reaction products were dissolved in water showed that the polycondensation reaction also takes place in aqueous solution, whereas dissolution in acetic dilute acid leads to complete stoppage of the polycondensation reaction and ensures more correct results. The polyalanine and diketopiperazine resulting from the reaction dissolve completely in 3% acetic acid as well as in water at any degree of completeness of the process, whereas the polymers obtained by heating D,L-valine, D,L-norleucine or glycine only dissolve up to the stage of 30-50% completion of the reaction. Their further heating leads to products with ever decreasing solubility in water and dilute acetic acid; their investigation therefore calls for a special technique whereas in the case of alanine such difficulties do not arise.

Water soluble products can be obtained by simultaneous polycondensation of two amino acid esters. Thus the separate heating of the ethyl esters of D,L-phenylalanine and glycine leads to water-insoluble polymers, whereas their joint polycondensation leads to formation of water-soluble products.

EXPERIMENTAL RESULTS

Investigation of the action of various additives on the reaction of polycondensation of the ethyl ester of D,L-alanine showed that considerable catalytic activity is manifested by acids such as carbonic, hydrochloric, sulfuric, acetic and propionic acids, as well as by polyalanine and aminoenanthic acid. Neutral and alkaline substances, such as diketopiperazine (lactimide), polyalanine ester, water, D,L-alanine, ammonia, diethylamine and KOH, do not bring about an appreciable increase in reaction velocity. Bearing in mind that esters of amino acids are them-

selves alkaline substances, it is clear that addition of amines and other bases cannot have an appreciable effect.

The catalysts which were most closely studied were carbon dioxide, acetic acid and polyalanine. In Table 1 are set forth the results of experiments on the polycondensation of the ethyl ester of D,L-alanine in presence of different amounts of carbon dioxide as a function of time at 55°, based on the change of content of free amino nitrogen as determined by the Van Slyke method and expressed as percentages of the original amino group content.

TABLE 1

Change of Content of Free Amino Groups in Percentages of the Original Content on Heating the Ethyl Ester of D, L-Alanine at 55° in Presence of Carbon Dioxide.

Duration of heating in hours	Amount of added carbon dioxide in wt. %					
	0.5	1.0	1.5	2.0	3.0	4.0
1	–	–	–	89.5	–	–
2	–	–	89.0	75.7	81.0	–
3	–	86.4	–	–	69.5	67.9
4	86.8	83.2	81.5	67.3	67.0	–
5	–	–	78.3	63.6	66.8	–
6	–	79.0	–	61.3	62.5	–
7	82.0	76.0	70.5	63.2	62.4	–
8	81.2	75.7	65.5	60.6	–	–
9	–	69.7	65.6	57.4	60.0	48.3
10	–	–	63.9	51.5	50.7	42.2
11		66.8	62.7	48.0	48.7	–
15	78.8	62.9	50.5	44.9	44.8	39.9

The result of polycondensation of the ester of D, L-alanine in presence of acetic acid and polyalanine are set forth in Table 2. This table also contains for comparison the results of polycondensation of this ester without catalysts. The acetic acid and polyalanine were used in the amount of 3%. Polyalanine was prepared by hydrolysis of its ethyl ester which had been obtained by polycondensation of the ethyl ester of D,L-alanine by heating in water at 80° for 20-30 minutes. The hydrolysis led to removal of a proportion of the ester groups with formation of terminal carboxyl groups. Such a polyalanine is essentially a high-molecular carboxylic acid and it is therefore not suprising that it should resemble acetic acid in its action. For comparison Table 2 also contains the results of experiments on the polycondensation of the ethyl ester of D, L-alanine in the absence of catalysts.

TABLE 2

Change of Content of Free Amino Groups as Percentage of the Original Content on Heating the Ethyl Ester of D,L-Alanine at 55° in Presence of Acids.

Duration of heating in hours	Name of catalyst		
	Acetic acid	Polyalanine	Without catalyst
3	74.7	72.0	–
4	–	–	98.4
6	68.5	67.4	–
7	66.0	65.5	–
8	–	–	97.7
10	60.2	62.8	95.6
13	52.1	61.7	–
15	–	–	97.4

It should be pointed out that in the first stages of the polycondensation, the polymers formed are soluble in the ethylester of D,L-alanine and the start of precipitation of the solid phase is the instant at which 75-80% of the original free amino groups are still intact (in the temperature range of 20-100°). On the basis of this observation, we can approximately estimate the velocity of the reaction resulting from the presence in the reaction mixture of a definite amount of catalyst. It was found that at 98° in the absence of catalysts, precipitation of solid phase only commences after 28 hours, whereas in presence of 2% carbon dioxide precipitation starts after 20 minutes. In this case, therefore, there is a 93-fold increase in reaction velocity.

As we have already indicated, the reaction products separate as solids which gradually fill the whole ampoule. After opening the ampoule and removing the alcohol in vacuum at room temperature, the reaction product is a brittle mass readily

pulverizable to a fine powder which melts at 260-280° with decomposition even in a sealed capillary. The polymers give the biuret reaction (red, blue and violet) and react with picric acid. It may be mentioned that when the polycondensation is performed in an aqueous medium, products are formed which give a red-violet biuret reaction, indicating the presence of a mixture of peptides of trimers and higher orders.

The ratio between the quantitites of linear polymer and cyclic dimer was determined in several reactions by sublimation in vacuum (0.1 mm) at 140°, as well as by ionophoresis by the method of Gavrilov and Balabukha [9]. It was found that the reaction temperature has the greatest influence upon the content of cyclic dimer in the reaction mass. Thus, in polycondensations performed at 55°, the dimer content as determined by the sublimation method was 35-40%, while at 100° it reached 70-80%. Determination by the ionophoresis method gives a lower content; thus, analysis of the product obtained at 55° by this method gave a value of only 26% dimer. This low value is possibly associated with thermal destruction of the polymer during sublimation of the dimer, leading to supplementary formation of cyclic dimer.

The occurrence of a catalytic action by carbon dioxide during polycondensation of esters of α-amino acids must be taken into account in connection with their storage. Thus, in a sealed ampoule filled in a carbon dioxide-free atmosphere, the ethyl ester of D, L-alanine is kept without appreciable change for up to two months, whereas in ampoules sealed in presence of air without special precautions, already on the fifth day the separation of solid is observed. The catalytic action of traces of carbon dioxide of the air is the cause of the instability of esters of α-amino acids in storage which has been noted by many authors and which had been attributed to the spontaneous tendency to polycondensation [2]. On the basis of our data, we may say that in the complete absence catalysts, the esters of α-amino acids can be kept unchanged for an unlimited period if kept out of contact with the air.

EVALUATION OF THE RESULTS OBTAINED

The considerable acceleration of polycondensation of esters of α-amino acids caused by acidic catalysts is of great interest in opening up new perspectives in the investigation of this type of reaction. Closer consideration of the experimental results, which are plotted in Fig. 4, enable us to see that the various catalysts differ slightly from one another in activity. Thus, carbon dioxide in the amount of 2% has a greater effect that 3% acetic acid. The amount of catalyst also influences the result. With increasing amount of carbon dioxide (this aspect was studied in more detail with this catalyst) the speed of transformation increases as shown in Fig. 4, where the top curve represents the velocity of the reaction without a catalyst. The optimum amount of carbon dioxide is evidently of the order of 2%. Further increase in the amount of carbon dioxide accelerates the reaction to a considerably smaller degree. The amount of combined amino groups, however, increases particularly sharply when the duration of the polycondensation is increased, as shown in Fig. 5 where the change in the amount of combined amino nitrogen is plotted as a function of the amount of carbon dioxide used in various periods of interaction.

The catalytic action of acidic catalysts is evidently associated with their ability to yield hydrogen ions which activate the ester bond and render it more reactive. As we know, the ester bond is extremely sensitive to the action of both acidic and alkaline catalysts, in whose presence all exchange reactions at ester bonds are sharply accelerated, as one of us showed in collaboration with Vinogradova [10]. In this connection it was established that acidic catalysts are more effective than alkaline catalysts. Since esters of α-amino acids are themselves strong bases, it is not surprising that in this case other bases do not exert an appreciable effect. At the same time the strong catalytic action of acids is understandable in view of their activation of the ester bond in esters of α-amino acids.

In this connection carbon dioxide occupies a somewhat special position since it is not a source of hydrogen ions. It is known, however, that amides are capable of combining with carbon dioxide to form salts of substituted carbamic acids. Frenkel and Katchalski [12] showed that esters of α-amino acids form with CO_2 salts of N-carboxy- α-amino acids:

$$2R-CH(NH_2)COOR' + CO_2 \rightleftharpoons R-\underset{\underset{COOR'}{|}}{CH}NHCOONH_2\underset{\underset{COOR'}{|}}{CH}-R\ .$$

It may be suggested that these salts, like salts of all other acidic catalysts, are formed when the catalysts are added to esters of amino acids and are catalysts of the process of polycondensation of esters of α-amino acids. Here we must point out that amino acids themselves, as we proved in the case of D, L-alanine, do not possess catalytic properties, this is probably bound up with the circumstance that the carboxyl group of amino acids, as is now

assumed [11], is linked with the amino group in the form of an inner salt (betaine form).

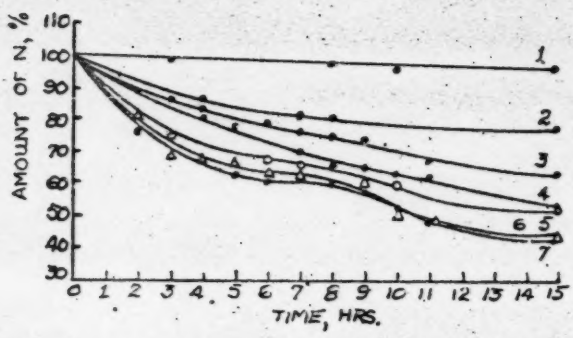

Fig. 4 Dependence of amount of nitrogen evolved in the Van Slyke analysis on the duration of the polycondensation of the ethyl ester of D,L-alanine; at 55°: 1) without catalyst; 2) in pressence of 0.5% CO_2; 3) in presence of 1% CO_2; 4) in presence of 1.5% CO_2; 5) in presence of 3% acetic acid; 6) in presence of 2% CO_2; 7) in presence of 3% CO_2.

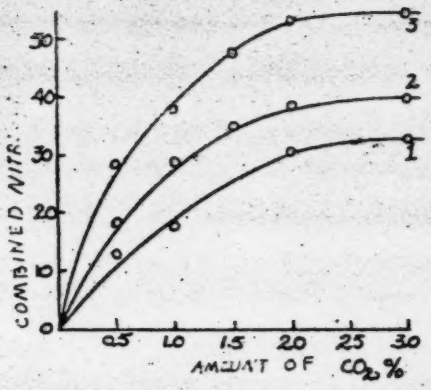

Fig. 5. Dependence of amount of combined amino nitrogen on the amount of added CO_2 in percentages of weight of ethyl ester of D,L-alanine: 1) for a reaction duration of 4 hours; 2) 8 hours; 3) 15 hours.

SUMMARY

1. The effect of various substances on the polycondensation of the ethyl ester of D,L-alanine was investigated.

2. Acids including carbonic acid in the form of carbon dioxide were found to sharply accelerate the polycondensation of esters of α-amino acids, whereas bases and amino acids are inactive.

3. The kinetics of polycondensation of the ethyl ester of D, L-alanine in presence of CO_2 and acetic acid and in the absence of catalysts was investigated.

4. It was established that with falling temperature the amount of cyclic dimer decreases and that of linear polymer increases in the polycondensation of the ethyl ester of D,L-alanine.

5. Co-polycondensation of ethyl esters of D,L-phenylalanine and glycine is shown to lead to formation of water-soluble products.

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HIGH MOLECULAR COMPOUNDS

COMMUNICATION 68. INVESTIGATION OF THE KINETICS OF COPOLYMERIZATION OF DIISOCYANATES WITH GLYCOLS

V. V. Korshak and I. A. Gribova

In the previous communication [1] we described the results of investigation of the process of copolymerization of diphenylmethane diisocyanate with 1,4-butanediol. It was found at the time that the molecular weight of the resultant polyurethan increases with increasing duration of the reaction as well as with rising concentration of the solution. The maximum molecular weight of the urethan is reached only over a specific temperature range [2]. The influence was investigated of excess of starting substances and of additions of such monofunctional substances as monohydric alcohols and amines, and it was shown that with increasing amount of additives the molecular weight of the resultant polyurethane decreases. It was established that polyurethans, like all heterochain polymers, are destroyed on heating with alcohols, carboxylic acid amides or isocyanates due to alcoholyis, aminolysis, acidolysis or isocyanolysis. It was suggested that these reactions may in certain conditions also play an important part in the process of synthesis of polyurethans [1, 2].

In this paper we present the results of investigations carried out on the kinetics of copolymerization of diphenylmethane diisocyanate with 1,4-butanediol in nitrobenzene solution.

EXPERIMENTAL

Experimental procedure. The kinetics of the reaction of diphenylmethane diisocyanate with 1,4-butanediol was studied at two concentrations: 0.0703 and 0.352 mole/l. A different procedure was applied for each concentration. In experiments in which the concentration of the starting substances was 0.0703 mole/l we used our previously described procedure [1]. The solution of the starting substances in nitrobenzene were heated in a thermostat at the experimental temperature, in the present instance 145°, and from the solution at definite time intervals were pipetted off 10 ml samples of the reaction mass. The samples were placed in a small flask with a ground glass stopper and cooled in snow to stop the reaction. Three 2 ml portions of the cooled reaction mass were then pipetted off. The content of free isocyanate groups was determined by titration with a chlorobenzene solution of dipropylamine by the method described below.

In experiments carried out with a concentration of starting substances of 0.352 mole/l the high viscosity of the reaction solution made it difficult to withdraw samples, and it was therefore necessary to conduct the reaction in ampoules. Weighed quantities of diphenylmethane diisocyanate and 1,4-butanediol and the requisite amount of nitrobenzene were placed in a flask with a ground-glass stopper and heated to 50° (at lower temperatures the 1,4-butanediol does not dissolve in nitrobenzene). After the 1,4-butanediol had dissolved, the hot solution was run into a series of 5 ml ampoules which were then sealed and placed in a thermostat heated to the required temperature, in this case 145 or 155°. At definite time intervals two ampoules were removed from the thermostat, quickly cooled in snow and opened; the contents of each ampoule were poured into separate flasks with ground-glass stoppers. Each ampoule was rinsed out with 10 ml nitrobenzene which was then added to the flask. The solution in the flask was titrated with a chlorobenzene solution of dipropylamine for determination of isocyanate groups by the method described below.

Determination of isocyanate groups. Into the flask containing the solution for analysis was run 5 ml 10% solution of dipropylamine in chlorobenzene. The mixture was stood on ice for 30 minutes. To the flask was then added 25 ml ethyl alcohol and 15 ml 0.5 N alcoholic NaOH in presence of a mixture of indicators (10 drops methylene blue and 5 drops methylene red). A blank determination was performed at the same time of the dipropylamine content of the chlorobenzene solution. The blank was titrated in the same manner as described above.

Determination of molecular weights of polyurethans from the content of terminal isocyanate groups. The sample of polyurethan to be analyzed for terminal isocyanate groups is subjected to the following preliminary treatment

for the purpose of keeping intact the isocyanate groups at the end of the chain and at the same time eliminating impurities. The hot reaction mass is poured from the flask into ten times the volume of dry acetone and the resultant precipitate is quickly filtered and dried in a vacuum-desiccator over phosphorus pentoxide. The dry powder is quickly pulverized in a mortar and sifted through a thick screen. A weighed amount of 1-2 g of the so-prepared polyurethan is placed in a flask with a ground-glass stopper to which are then added 3 ml of a 10% solution of piperidine in chlorobenzene and 10 ml chlorobenzene to ensure that the sample of polymer is completely covered with a layer of liquid. The flask is placed in a thermostat and heated at 80° for 30 minutes. The flask was then withdrawn and cooled in ice. The unreacted piperidine is back-titrated with 0.1 N alcoholic HCl in presence of 10 drops methylene blue and 5 drops methylene red. At the same time a blank titration is performed on the original solution of piperidine in chlorobenzene. The difference between the number of milliliters of 0.1 N HCl consumed in titration of the piperidine in the blank and in the presence of polyurethan corresponds to the number of isocyanate groups. The calculation of the molecular weight of products obtained with use of excess of diisocyanate made allowance for the presence of isocyanate groups at both ends of the molecule [3], using the formula:

$$M = \frac{20\,000 \cdot a}{b \cdot k},$$

where M is the molecular weight of the polyurethane; a is the weight of the polyurethan sample, in g; b is the consumption of 0.1 N HCl in milliliters, 20,000 is the number of milliliters of 0.1 N HCl required for one mole of polyurethan. K = correction later for HCl. In Table 1 are set forth examples of determination of molecular weight of polyurethans on the basis of the number of terminal isocyante groups and of the viscosity.

TABLE 1

Comparison of molecular weights of polyurethans as determined from the number of terminal isocyanate groups and from the viscosity

Excess of diisocyanate in mole-%	Mol. wt. from no. of end groups	Viscosity of 0.5% solution in phenol (80%)	Mol. wt. determined from the viscosity
11.0	11 580	0.2063	12 720
11.0	12 380	0.2063	12 720
18.4	11 480	0.1991	12 330

Results obtained. Results of experiments with concentration of 0.0703 mole/l of the starting solution at 145° are set forth in Table 2.

Experiments with a concentration of 0.352 mole/l were performed by the other method due to the high viscosity of the solution, as mentioned above, at temperatures of 145 and 155°. The results are set forth in Tables 3 and 4.

TABLE 2

Kinetics of the reaction of diphenylmethane diisocyanate with 1,4-butanediol at 145° and conc. of 0.0703 mole/l

Duration in min.	Degree of completeness of reaction p	Extent of reaction c_p	x in mole-%	(a − x) mole-%	$\frac{x}{(a-x)\,a}$	K in l/mole min.
10	0.295	1.41	0.0221	0.0482	6.54	0.651
20	0.355	1.55	0.0261	0.0442	8.42	0.421
30	0.417	1.71	0.0304	0.0399	10.83	0.361
60	0.523	2.10	0.0376	0.0327	16.38	0.273
120	0.706	3.40	0.0502	0.0201	35.48	0.295
180	0.797	4.90	0.0564	0.0139	59.18	0.328

In addition to determination of the amount of starting materials after various intervals of time, which gave the reaction velocity as a function of the reaction temperature and the concentration of starting substances, we determined the molecular weight of the polyurethans formed. The results are set forth in Table 5, in which for comparison is included the degree of completeness of the reaction at various intervals of time.

Evaluation of results obtained. The results of our investigation of the reaction of diphenylmethane diisocyanate with 1,4-butanediol, set forth in Tables 2 to 5, permit us to draw a series of important conclusions about the kinetics of the reaction of diisocyanates with glycols and about the mechanism of this reaction. We shall first consider the influence of the concentration of the starting substances.

TABLE 3

Kinetics of reaction of diphenylmethane diisocyanate with 1,4-butanediol at 145° and a conc. of 0.352 mole/l

Duration in min.	Degree of completeness of reaction p	Extent of reaction c_p	x in mole/l	(a − x) mole/l	$\frac{x}{(a-x)\,a}$	K in l/mole min.
10	0.826	5.6	0.2958	0.0564	14.88	1.488
20	0.870	7.6	0.3066	0.0457	23.95	1.150
30	0.872	7.8	0.3151	0.0372	24.02	0.800
60	0.938	16.1	0.3305	0.0218	43.07	0.720
120	0.965	28.5	0.0340	0.0122	78.86	0.650
300	0.965	28.5	0.0340	0.0122	78.86	0.650

TABLE 4

Kinetics of reaction of diphenylmethane diisocyanate with 1,4-butanediol at 155° and conc. of 0.352 mole/l

Duration in min.	Degree of completeness of reaction p	Extent of reaction c_p	x in mole/l	(a − x) mole/l	$\frac{x}{(a-x)\,a}$	K in l/mole min.
10	0.827	5.7	0.2931	0.0607	13.363	1.363
20	0.882	8.4	0.3123	0.0415	21.3	1.06
30	0.923	12.9	0.3267	0.0271	34.0	1.13
60	0.956	22.7	0.3382	0.0155	61.4	1.02
120	0.976	41.7	0.3459	0.0079	123.4	1.03
300	0.995	–	–	–	–	–

TABLE 5

Change of molecular weight of polyurethans in dependence on the reaction temperature at a conc. of 0.352 mole/l

Duration in min.	Reaction temperature					
	145°			155°		
	Degree of completeness of reaction p	Viscosity of 0.5% solution in aq. phenol	Mol. wt. of polyurethan	Degree of completeness of reaction p	Viscosity of 0.5% solution in aq. phenol	Mol. wt. of polyurethan
10	0.826	–	–	0.827	–	–
20	0.870	–	–	0.882	–	–
30	0.872	0.082	5 000	0.923	0.105	6 500
60	0.938	0.109	6 700	0.956	0.134	8 300
90	–	0.132	8 200	–	0.153	9 500
120	0.965	–	–	0.976	–	–
180	–	0.167	10 300	–	0.212	13 200
300	0.965	0.203	12 600	0.995	0.244	15 200

As we see from Fig. 1, with rise of concentration of the initial reactants (at the same temperature of 145°) there is a considerable increase in reaction velocity which enables a degree of completeness of the reaction of 0.826 to be reached at a concentration of 0.352 mole/l in 10 min. whereas at a concentration of 0.0703 mole/l this degree of completeness requires 180 minutes.

Fig. 2 illustrates the change of extent of reaction (c_p) as a function of the concentration and reaction of temperature.

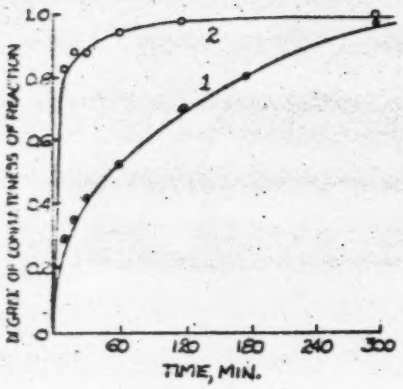

Fig. 1 Kinetics of copolymerization of diphenylmethane diisocyanate with 1,4-butanediol at 145°. 1) Conc. of starting substances 0.0703 mole/l; 2) conc. of starting substances 0.352 mole/l.

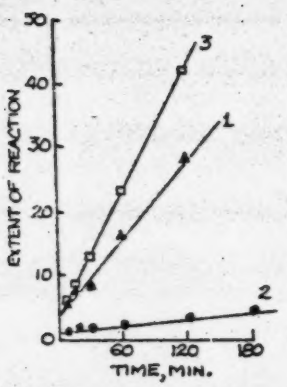

Fig. 2. Change of extent of reaction of copolymerization of diphenylmethane diisocyanate with 1,4-butanediol at various concentrations and temperatures: 1) 145°, 0.3523 mole/l; 2) 145°, 0.07028 mole/l; 3) 155° 0.3538 mole/l.

It is clear from the graph that the extent of reaction, denoting the ratio of the initial number of functional groups introduced into the reaction to the number of functional groups at the given instant ($c_p = N_0/N$), also increases with the concentration and temperature of the reaction.

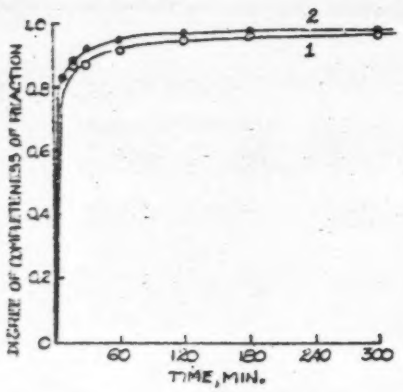

Fig. 3. Dependence of degree of completeness of the reaction on the duration of the experiment: 1) at 145°; 2) at 155°.

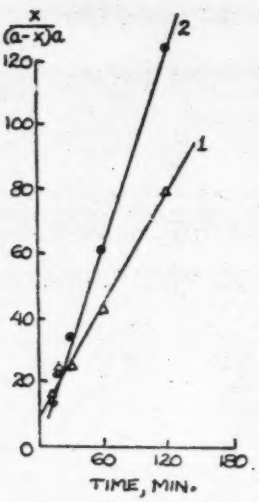

Fig. 4. Graphical determination of velocity constants at a conc. of starting substances of 0.253 mole/l: 1) At 145°; 2) at 155°.

The influence of the reaction temperature at a concentration of the initial substances of 0.352 mole/l is shown in Fig. 3.

We see from Fig. 3 that a 10° rise of temperature (from 145 to 155°) leads to appreciable acceleration of the reaction.

We determined the order of the reaction (van't Hoff) (see Tables 2,3, and 4) and found that the reaction of diphenylmethane diisocyanate with 1,4-butanediol is of the second order as a bimolecular reaction. The mean value of the velocity constants was determined from the tangent of the angle of slope of the straight line obtained by plotting (ordinates) the value of $\frac{x}{(a-x)a}$, against (abscissas) time. The mean value of the constants at 145° was found to be 0.571 liters/(moles · min.), while at 155° the value was unity. The graphs from which the mean values of the constants were determined are plotted in Fig. 4.

The data obtained were used to calculate the temperature coefficient of the reaction; for the range 145-155° it was found to be 1.751. The activation energy of the reaction of diphenylmethane diisocyanate with 1,4-butanediol was found to be 19,900 cal/mol.

The data of Table 5 were applied to the construction of the curves shown in Fig. 5; these show the change in molecular weight of the formed polyurethan during the reaction and the simultaneous change in the degree of completeness of reactions, i.e. the rate of consumption of the starting substances.

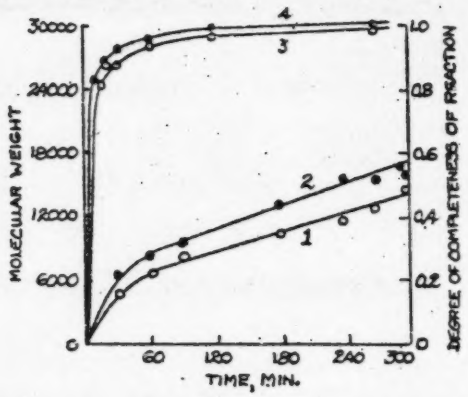

Fig. 5. Dependence of molecular weight 1) At 145°; 2) at 155°) and degree of completeness of reaction 3) at 145°; 4) at 155°) on the duration of an experiment.

Inspection of these curves enables us to draw some extremely important conclusions regarding the growth of the polyurethan molecule during the reaction. On comparing curves 1 and 2 (relating to 145°) with curves 3 and 4 (relating to 155°), it is easy to see that there is no complete correlation between the degree of completeness of the reaction and the rise of molecular weight of the polyurethan. After a period of only 60 minutes, 94-96% of the starting substances has been consumed but the molecular weight in spite of this continues to rise twice as much in the following 240 minutes although the change in the amount of starting materials over this period is only 2.5-3.5%. Consequently the growth of the polyurethan molecule during the latter stages of the reaction does not involve molecules of the initial monomers but is the result of interaction between the macromolecules.

This conclusion is fully consistent with the results of investigation of the polycondensation of 1,6-hexanediol with sebacic acid which one of us carried out in collaboration with Vinogradova [4]. This investigation also revealed that the starting monomers disappear in the very first stages of the reaction, notwithstanding which the growth of molecules of the polyester continues subsequently by interaction of the macromolecules among themselves.

This conclusion has considerable significance for the understanding of many chemical reactions of high-molecular compounds, since it shows that macromolecules possess considerable mobility and consequently considerable reactivity. This aspect must be taken into account in all cases. Reactions between macromolecules can evidently have great importance in various processes, including polymerization.

In conclusion we shall consider briefly some characteristics of the reaction of diisocyanates with glycols. Regarding, first of all, the known analogy between reactions of diisocyanates and those of ketenes, this similarity can be understood if we take into account the fact that ketenes are inner anhydrides of carboxylic acids:

$$R - CH\overset{H}{\underset{}{\vert}}\!\!\left[\!\!\begin{array}{l}\!\!-CO-\\ \!\!-OH\end{array}\right]\!\!\cdot,$$

while isocyanates can likewise be regarded as inner anhydrides of carbamic acids:

$$R-N\boxed{H-CO-OH}$$

This analogy harmonizes with the close similarity in the reactions of isocyanates and ketenes, as manifested by the fact that the most typical reactions of both classes of compounds are addition reactions at the double bonds of various substances containing mobile hydrogen atoms, such as alcohols, acids and amines, or polymerizations (which are essentially additions between like molecules). Consequently the following considerations about reactions of isocyanates are evidently applicable in equal measure to reactions of ketenes.

It may be suggested that the carbon-nitrogen double bond in isocyanates is strongly polarized under the influence of the oxygen atom and therefore tends strongly to link with polarized molecules according to the scheme:

$$R-N=\overset{\delta+}{C}=O+R^{I}\overset{\delta-}{O}-\overset{\delta+}{H}\rightarrow R-NH-COO-R^{I}.$$

This accounts for the fact that the reaction of isocyanates with glycols and, in particular, with the more strongly polarized amines, proceeds extremely rapidly with a velocity typical of ionic reactions.

SUMMARY

1. The kinetics of the reaction of copolymerization of diphenylmethane diisocyanate with 1,4-butanediol was investigated at 145 and 155° in nitrobenzene solution at concentrations of 0.352 and 0.0703 mole/1.

2. A study was made of the dependence on time of the growth of molecular weight of the polyurethan during copolymerization of diphenylmethane diisocyanate and 1,4-butanediol.

3. It was found that increasing concentration of the starting substances and rising temperature speed up the copolymerization of diisocyanates with glycols.

4. The molecular weight of the polyurethan formed is found to rise with increasing concentration of starting substances and rising temperature.

5. In the later stages of copolymerization of diisocyanates with glycols the rise of molecular weight is mainly due to mutual interaction of the pdyurethan macromolecules.

6. A new method of determination of molecular weight of polyurethans is based on determination of the terminal isocyanate groups.

7. Determinations were made of the velocity constants, temperature coefficients and activation energies of the reaction of diphenylmethane diisocyanate with 1,4-butanediol.

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* See Consultants Bureau Translation, p. 467.

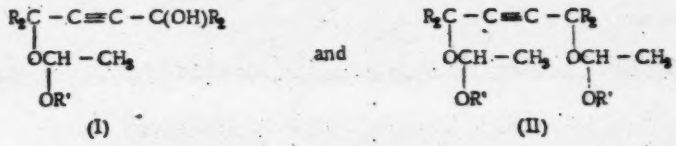
** " " " " , p. 967.

INVESTIGATION OF ACETYLENIC ALCOHOLS AND GLYCOLS

COMMUNICATION 3. STEPWISE SYNTHESIS OF ACETALS OF ACETYLENIC GLYCOLS

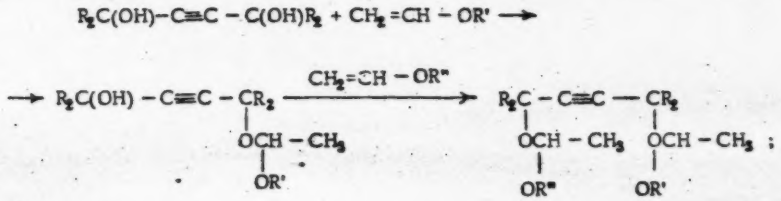
M. F. Shostakovsky and A. V. Bogdanova

The synthesis and investigation of the properties of acetylenic glycols are of undoubted interest in view of their great reactivity. In previous communications [1, 2] methods were presented for synthesis of mono- and dialkyl acetals of acetylenic alcohols with the general formulas:



(I) and (II)

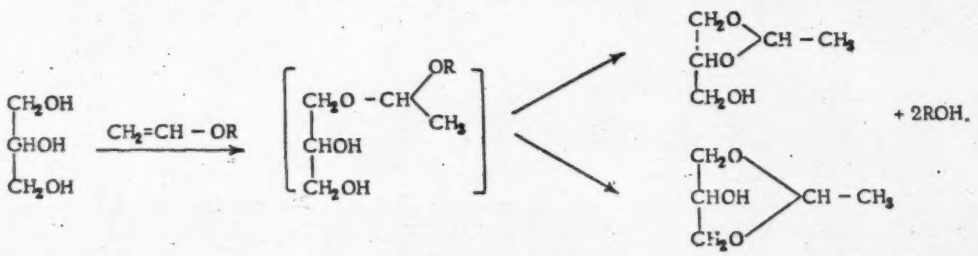
The new substances which have been synthesized and the methods for their synthesis are of interest for acetylene chemistry. As was previously observed [1, 2], the synthesis of diacetals of acetylenic glycols is always accompanied by formation of the corresponding monosubstituted acetals. For this reason we suggested that a stepwise reaction was involved, i.e. that the monoacetal formed in the first step may either be isolated or (if left in the reaction medium) may join on with another molecule of vinyl ether to form the diacetal in accordance with the following equations:



where R' and R" = C_2H_5; C_4H_9; C_8H_{17}.

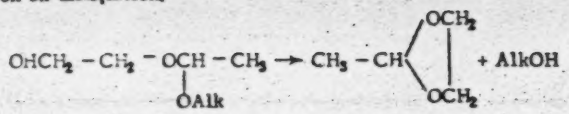
The stepwise mechanism of the synthesis enables two series of derivatives of acetylenic glycols to be obtained: mono- and diacetals. Most of the known derivatives of acetylenic glycols are disubstituted compounds [3, 4]. Monosubstituted acetylenic derivatives reported in the literature are the partial ethyl and isoamyl ethers of tetramethylbutynediol which were prepared and examined by Zalkind [5]. It is interesting that the formation of monoacetals of the type of (I), as well as of mixed acetals, is only found possible for the acetylenic glycols series. In the case of saturated or of olefinic glycols, as well as of glycerol and other polyhydric alcohols, attempts to separate the mono- and diacetals have proved unsuccessful due to cyclization [6, 7, 8, 9].

In the case of glycerol [8] this process takes place according to the scheme:



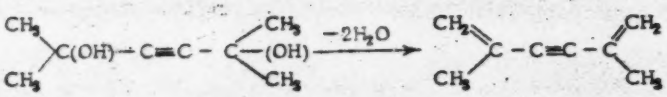
Reaction of ethyleneglycol with vinyl ethers usually leads to dicyclic acetals [9], and only the application of exceptional synthesis conditions (excess of vinyl ether, a strict temperature limit and absence of acid catalyst) enabled this author to partly avoid cyclization. The isolated ethylene glycol monoacetals, however, proved to be very

unstable and underwent cyclization on distillation:



Dehydration of tetramethyl- and tetraphenylbutynediols [10, 11] was observed on their condensation with phenol; during this process the phenol added on to the triple bond of the glycol.

The literature also contains earlier reports of the hindering effect of the triple bond, for example during dehydration of acetylenic glycols [12]. In this case, instead of the cyclization which occurs with saturated pinacones, formation takes place of unsaturated hydrocarbons:

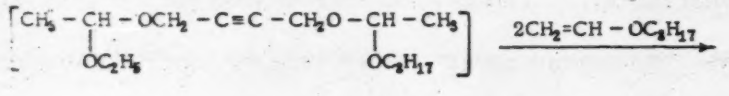


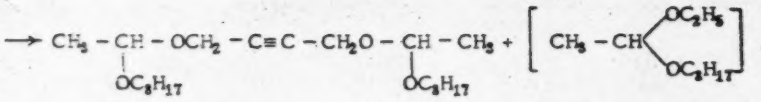
Similarly a study of the magnetic fields of acetylenic hydroxyl-containing compounds [13] revealed the screening effect of the triple bond.

Investigations by Favorsky and his school [14, 15, 16] demonstrated the possibility of existence of carbocyclic systems with a triple bond, starting only from an 8-membered ring. Cyclization of monoacetals of acetylenic glycols is also excluded by the circumstance that the triple bond creates a great strain in the hydrocarbon chain of the molecule, hindering the cyclization which might have led to formation of only a 7-membered ring.

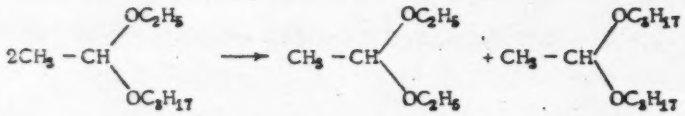
In this communication experimental confirmation is given of the stepwise formation of diacetals of acetylenic glycols with reference to the diethyl, ethylbutyl and dioctyl acetals of butynediol.

Stepwise synthesis of the diacetals was realized by two methods: catalytic and thermal. By these methods the corresponding diacetals were isolated from the mono- acetals in good yields. An attempt to obtain the mixed ethyloctyl diacetal of butynediol led to isolation of the symmetrical diethyl acetal whose formation may be explained by a process of symmetrization of the mixed diacetal formed in the first step:





Symmetrization of the mixed ethyloctyl acetal of acetaldehyde gives, in accordance with the following scheme, the acetaldehyde dioctyl acetal which we isolated:



It is interesting that symmetrization was observed mainly in the case of butynediol ethyloctyl diacetal and to a lesser degree in that of butynediol ethylbutyl diacetal. Such a difference in behavior is probably to be explained by the large difference in molecular weights of the alkoxy radicals simultaneously present in the molecule of the diacetal: the greater this difference the less stable is the molecule of mixed acetal and the greater the tendency to symmetrization.

EXPERIMENTAL *

The starting vinyl ethers were purified by the previously described method [14] and had the constants set forth in Table 1. The butynediol had b.p. 142-143° (14 mm); b.p. 57-58°.

1. Stepwise synthesis of the diethylacetal of butynediol $C_2H_5O - (CH_3)CHO - CH_2 - C \equiv C - CH_2 - OCH(CH_3) - OC_2H_5$.

Preparation of butynediol monoethylacetal by the thermal method. Heating in an autoclave to 81-88° of a

* Senior laboratory technician M. S. Egorova participated in the experimental work.

mixture of 43 g (0.5 mole) butynediol and 37 g (0.5 mole) vinylethyl ether for 2 hours followed by vacuum distillation gave 60.2 g (77.0% of the theoretical) of the monoethyl acetal of butynediol with constants (Table 2) in accordance with the literature [1].

TABLE 1

Constants of initial vinyl ethers

No.	Ether	B.p. in °C (p in mm Hg)	n_D^{20}
1	Vinylethyl	36.0-36.5	1.3785
2	Vinylbutyl	93.0-93.5	1.4035
3	Vinyloctyl	59-60 (10 mm)	1.4275

Preparation of butynediol diethylacetal from the monoacetal by the thermal method. Into a stainless steel bomb of 300 ml capacity were charged 33.5 g butynediol monoethylacetal and 17.0 g vinylethyl ether. The bomb was heated on an oil bath to 100-105° for 12 hours. 49.6 g light-yellow product was discharged and on vacuum fractionation gave the following fractions:

Fraction I, B. p. to 137° (33-18 mm): 8.2 g
Fraction II, B. p. 137-138° (18 mm): 35.3 g
Residue 4.9 g

Fraction I contained unreacted vinylethyl ether with b.p. 36.0-36.5° and n_D^{20} 1.3775.

Fraction II was the diethylacetal of butynediol with constants (Table 2) agreeing with the literature [1]. Its yield was 72.4 % of the theoretical.

TABLE 2

Constants of the prepared acetals

No.	Formula of acetal	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
1	$HO-CH_2-C\equiv C-CH_2-OCH(CH_3)-OC_2H_5$	127-128 (11)	1.4550	1.0188
2	$CH_3-\underset{\displaystyle OC_2H_5}{\underset{\vert}{CHO}}-CH_2-C\equiv C-CH_2-\underset{\displaystyle OC_2H_5}{\underset{\vert}{OCH}}-CH_3$	137-138 (18)	1.4400	0.9743
3	$CH_3-\underset{\displaystyle OC_2H_5}{\underset{\vert}{CHO}}-CH_2-C\equiv C-CH_2-\underset{\displaystyle OC_4H_9}{\underset{\vert}{OCH}}-CH_3$	141-142 (6)	1.4420	0.9595
4	$CH_3-CH\begin{matrix}OC_8H_{17}\\OC_8H_{17}\end{matrix}$	150-151.5 (7)	1.4315	0.8408
5	$CH_3-\underset{\displaystyle OC_8H_{17}}{\underset{\vert}{CHO}}-CH_2-C\equiv C-CH_2-\underset{\displaystyle OC_8H_{17}}{\underset{\vert}{OCH}}-CH_3$	161-165 (0.05)	1.4500	0.9150

Preparation of diethylacetal of butynediol from the monoacetal by a catalytic method. To a solution of 20 g monoethylacetal of butynediol in 20 g dioxane in presence of 3 drops conc. hydrochloric acid was added dropwise, with stirring, 11.0 g vinylethyl ether. The addition was accompanied by rise of temperature to 30°. The subsequent heating was carried out at 48-50° for 4 1/2 hours. The outwardly unchanged solution was treated with potassium carbonate and left overnight. After filtration and distillation of the dioxan, vacuum distillation gave 28.7 g diethylacetal of butynediol with the constants: b.p. 140-141° (20 mm); n_D^{20} 1.4395; d_4^{20} 0.9727; yield 98.3% of the theoretical.

II. Stepwise snythesis of the ethylbutyl diacetal of butynediol [$C_2H_5O(CH_3)CHO-CH_2-C\equiv C-CH_2-OCH(CH_3)-OC_4H_9$]

Preparation of butynediol monoethylacetal. The preparation was described above.

Preparation of ethylbutylacetal of butynediol from the monoethylacetal by the catalytic method. To a

solution of 15.8 g butynediol monoethylacetal in 10 g dioxan in presence of a drop of conc hydrochloric acid at room temperature was added 12.0 g vinylbutyl ether. The mixture was then heated for 3 hours at 40°; the dioxan was driven off and the residue fractionated in vacuum:

Fraction I	B. p. 130-154° (13 mm);	9.7 g
Fraction II	B. p. 154-162° (13 mm);	6.5 g
Residue		7.5 g

From Fraction I was recovered 3 g unchanged butynediol monoethylacetal with the constants: b.p. 130-131° (14 mm); n_D^{20} 1.4550; d_4^{20} 1.0185.

From Fraction II was separated 4.5 g of a product with the constants: b.p. 141-142° (6 mm); n_D^{20} 1.4420; d_4^{20} 0.9595, found MR 71.23; calculated MR 71.36

	Found %:	C 64.45; 64.38; H 9.91; 9.98
$C_{14}H_{26}O_4$.	Calculated %:	C 64.83; H 10.09
	Found M:	238.90
$C_{14}H_{26}O_4$	Calculated M:	258.35

Hydrolysis and acetal determination (methods described in [1, 2]): 97.2; 98.0%.

The constants and analysis of the isolated product identify it as butynediol ethylbutyl diacetal. Its yield is 28.1% of the theoretical. Butynediol ethylbutyl diacetal was also prepared by the thermal method, by heating equimolar amounts of butynediol monoethyl acetal and vinylbutyl ether at 115-120° for 12 hours in a bomb.

III. Reaction of butynediol monoethyl acetal with vinyloctyl ether

$[C_2H_5OCH_2CHO - CH_2 - C \equiv C - CH_2OCH(CH_3) - OC_8H_{17}]$

The starting material for this synthesis was the above-described butynediol monoethyl acetal. To a solution of 25.3 g butynediol monoethyl acetal in 23 g dioxan in presence of 3 drops conc. HCl was added dropwise at 60-65° 26 g vinyloctyl ether. The mixture was then heated to 80-85° for 16 hours; the dioxane was driven off and the residue fractionated in low vacuum:

Fraction I	B. p. 122-155° (6 mm),	30.0 g
Fraction II	B. p. 155-185° (10 mm),	13.4 g
Residue		7.0 g

Refractionation of Fraction I gave 7.5 g of a product with the following constants: b.p. 150-151.5° (7 mm); n_D^{20} 1.4315, d_4^{20} 0.8408; found MR 88.29; calculated MR 88.61.

	Found %:	C 74.84; 74.93, H 13.20; 13.32
$C_{18}H_{38}O_2$.	Calculated %:	C 75.46; H 13.37
	Found M:	268.1; 274.1
$C_{18}H_{38}O_2$	Calculated M:	286.48

The constants and analysis of the isolated product identify it as acetaldehyde dioctyl acetal [17]. Yield 15.7% of the theoretical.

From Fraction II was isolated 10 g of product with the constants: b.p. 161-165° (0.05 mm); n_D^{20} 1.4500; d_4^{20} 0.9150; found MR 116.9, calculated MR 117.10. (Even in high vacuum the product distils with slight decomposition.)

	Found %:	C 71.81; 71.67; H 11.54; 11.38
$C_{24}H_{46}O_4$.	Calculated %:	C 72.31; H 11.63
	Found M:	349.30; 336.50
$C_{24}H_{46}O_4$.	Calculated M:	338.61

Hydrolysis and acetal determination: 97.57; 96.62%.

The constants found and the analysis enable us to regard the isolated product as butynediol dioctyl acetal. Yield 15.1% of the theoretical.

SUMMARY

1. The stepwise mechanism of the addition of vinyl ethers to acetylenic glycols was confirmed.

2. The intermediate products of this reaction – monoacetals of acetylenic glycols – were isolated in good yields both by thermal and by catalytic methods.

3. The following corresponding diacetals were prepared from the monoacetals of acetylenic glycols by various methods: diethyl, ethylbutyl and dioctyl; the two latter were prepared for the first time.

4. It was demonstrated that in the preparation of mixed diacetals from the corresponding monoacetals, the main reaction is accompanied by a process of symmetrization which is intensified with increasing difference between the molecular weights of the radicals of the starting vinyl ethers. The result of this process is the formation of a symmetrical diacetal consisting of the product of substitution of the low-molecular alkoxy group by the higher molecular one.

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INVESTIGATIONS OF THE INTERACTION BETWEEN VINYL AND POLYFUNCTIONAL COMPOUNDS

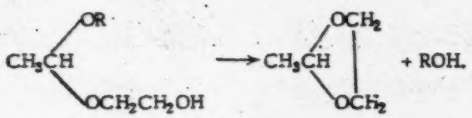
COMMUNICATION 3. REACTION OF GLYCEROL TRIVINYL ETHER WITH ETHYLENE GLYCOL AND 1,4-BUTANEDIOL

M. F. Shostakovsky, V. V. Zhebrovsky and M. A. Medelyanovskaya

In previous communications on the reaction of vinyl ethers with glycerol [1] and with polyvinyl alcohol [2] it was established that the reaction always proceeds with formation of the corresponding cyclic acetals.

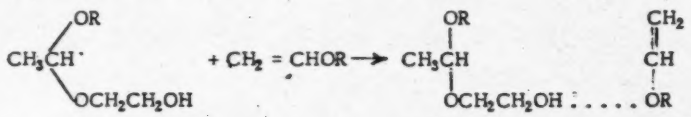
The present investigation is devoted to a study of the course of the reaction in the case when both components are polyfunctional compounds, using glycerol trivinyl ether and glycols (ethylene glycol and 1,4-butanediol) as models. It has been shown [3] that in many reactions the interaction of the hydroxyl groups of ethylene glycol proceeds either stepwise or simultaneously, thus necessitating the selection of appropriate conditions for preparing its mono- and difunctional derivatives.

In the interaction of ethylene glycol with alkylvinyl ethers the formation of monoalkyl acetals is observed on heating, whereas the corresponding dialkyl acetals of ethylene glycol are predominantly formed in presence of a catalyst. At the same time the monoacetals are found to be easily transformed into cyclic acetals:



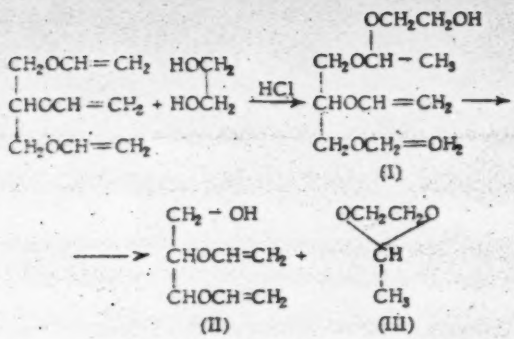
The ratio of starting components is of great importance. Thus, molar ratios (1:1) of vinyl ether and ethylene glycol lead to monoalkyl acetals, whereas with equivalent (2:3) amounts of reactants the corresponding cyclic acetal is formed.

Dialkyl acetals of ethylene glycol are obtained by reacting the latter with excess of the vinylalkyl ether in presence of a catalyst. The excess of the vinyl ether is an important factor since the reversal of the order of addition of the reactants leads to the reaction being shifted in the direction of cyclization of the monoacetal. The authors believe that this is due to the fact that acetalization of one hydroxyl group of ethylene glycol enhances the activity of the hydrogen of the remaining hydroxyl group, leading to cyclization of the monoacetal with separation of the alcohol. In presence of an excess of vinyl ether, however, the transformation of the monoacetal into a cyclic acetal is hindered by formation of a hydrogen bond.



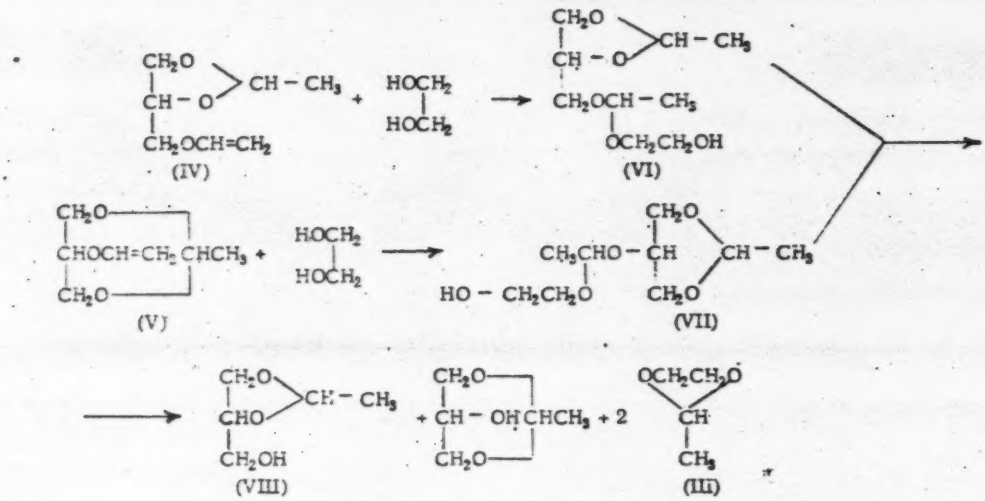
Formation of acetals of glycols containing free hydroxyl groups was observed in the case of unsaturated glycols. In the latter the factor hindering cyclization is the presence of a triple bond. In an investigation of the reaction of vinyl ethers with tetramethylbutynediol and 1,4-butynediol, one of us in collaboration with Bogdanova [4, 5] did not isolate the cyclic acetals; the reaction yielded the mono- and diacetals of tetramethylbutynediol and 1,4-butynediol, and it was observed that the formation of diacetals proceeds through the stage of formation of monoacetals whose yield depends on the synthesis conditions.

In the present investigation of the reaction of glycerol trivinyl ether with ethylene glycol and 1,4-butanediol, it was found that the inevitable product of the first stage of reaction of glycerol trivinyl ether with ethylene glycol in molar ratios was the mixed acetal of glycerol vinyl ether and ethylene glycol (I).

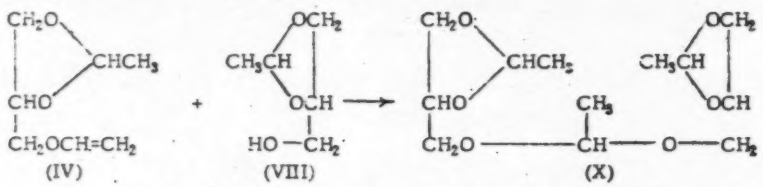


which, being unstable, breaks down to the partial vinyl ether of glycerol (II) and the cyclic acetal of ethylene glycol (III).

Isomerization of the divinyl ether of glycerol (II) leads to formation of the 1,2- and 1,3-acetals of the mono vinyl ether of glycerol (IV) and (V). The latter react with ethylene glycol to form the mixed acetals (VI) and (VII) which break down to 1,2- and 1,3-acetals of glycerol (VIII) and (IX) and the acetal of ethylene glycol (III):



The isomeric acetals (VIII) and (IX) are separated by taking advantage of the different solubilities of their benzoates in low-boiling gasolines. The triacetal of glycerol was also isolated during the investigation; its formation could result from interaction of acetals (IV) and (VIII):

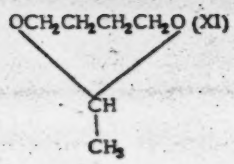


With equimolar ratios of glycerol trivinyl ether and ethylene glycol (2:3) the reaction mainly proceeds with formation of the cyclic acetals of glycerol and ethylene glycol (III) and (VIII).

The formation of a minor amount of glycerol 1,3- acetal (IX) may be explained in the following manner: reaction of glycerol trivinyl ether with ethylene glycol gives in the first instance a mixed acetal involving the α-vinyl group of the ether; this mixed acetal evidently then breaks down to the 1,2-divinyl ether of glycerol which isomerizes to the monovinyl ether of glycerol 1,2-acetal owing to the spatial closeness of the free primary OH group to the vinyl group in the α-position.

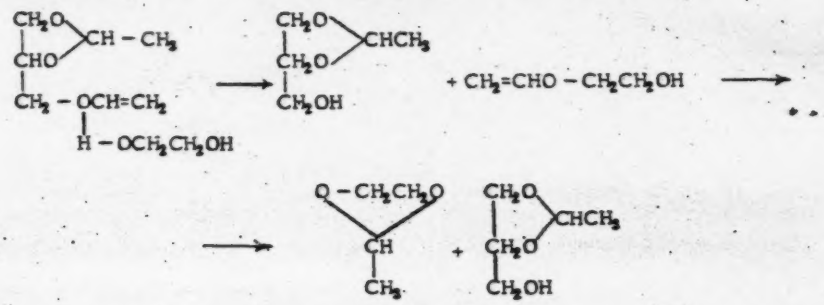
In the interaction of glycerol trivinyl ether with 1,4-butanediol, using molar ratio of components, cyclic acetals are evidently formed according to the same scheme as for ethylene glycol. We actually isolated

the cyclic acetal of 1,4-butanediol:



the two glyceryl acetals (VIII) and (IX) and the glyceryl triacetal (X).

Formation of cyclic acetals of ethylene glycol and 1,4-butanediol can be explained by the following mechanism: After establishment of a hydrogen bond between the oxygen of the 1,2-glyceryl acetal and the hydrogen of ethylene glycol or 1,4-butanediol vinyl rearrangement proceeds according to the scheme:



Consequently the formation of cyclic acetals of ethylene glycol and 1,4-butanediol is accompanied by indirect vinylation of the latter.

EXPERIMENTAL

The glycerol trivinyl ether was prepared by the method of Favorsky and Shostakovsky and had b.p. 164-165°; n_D^{20} 1.4382, d_4^{20} 1.03325; the ethylene glycol had b.p. 196-196.5°; n_D^{20} 1.4279; the 1,4-butanediol had b.p. 117-118° (7-8 mm); n_D^{20} 1.4470.

Reaction of glycerol trivinyl ether with ethylene glycol in molar ratio.

42.5 g (0.25 mole) glycerol trivinyl ether and 15.5 g (0.25 mole) ethylene glycol were mixed for 1/2 hour; the catalyst consisting of 2 drops (0.028 g) hydrochloric acid was then introduced; the reaction took place instantaneously with rise of temperature to 92°. After neutralization with potassium carbonate the product was distilled from a Favorsky flask, the following fractions being obtained from the 51.88 g material in the flask:

Fraction I	B.p. 70-80°		1.45 g;	
Fraction II	B.p. 81-83°		18.08 g;	n_D^{20} 1.4008
Fraction III	B.p. 83-100°;	(11-12 mm);	24.97 g;	n_D^{20} 1.4452
Fraction IV	B.p. 157-166°;	(11-12 mm);	4.98 g;	n_D^{20} 1.4496
Fraction V	B.p. 170°	(11-12 mm);	0.76 g;	n_D^{20} 1.4520
Residue from distillation			1.52 g;	n_D^{20} 1.4615

a) Redistillation of Fraction II gave 6.76 g substance with b.p. 81-82°; d_4^{20} 0.9858; n_D^{20} 1.3999, corresponding to the cyclic acetal of ethylene glycol (III).

The literature data [6] are: b.p. 82.3°; d_4^{24} 0.9770; n_D^{24} 1.3945.

Found M 87.60
Calculated M 88.10

Found MR 21.53
$C_4H_8O_2$. Calculated MR 21.76

Found %: C 54.03; 53.75; H 9.30; 9.18
$C_4H_8O_2$. Calculated %: C 54.54 H 9.09

b) Fraction III reacted with metallic sodium and methylmagnesium iodide and was subjected to benzoylation. To a mixture of 20 g Fraction III and 48 g pyridine (b.p. 114-115°) was gradually added 83.7 g benzoyl chloride (b.p. 75-76°) (10-11 mm). The reaction gave 8.42 g crystalline 1,3-ethylideneglyceryl benzoate and 11.36 g liquid 1,2-ethylideneglyceryl benzoate, in all 23.92 g (52.6% of the theoretical) [1].

Crystalline 1,3-ethylideneglyceryl benzoate had the constants: m.p. 84-85°; found M 224.1; calculated M 222.23.

	Found %:	C 65.03; 65.26;	H 6.31; 6.25
$C_{12}H_{14}O_4$	Calculated %:	C 64.86;	H 6.31

1,2-Ethylideneglyceryl benzoate had the constants: b.p. 179-180° (17 mm); d_4^{20} 1.1556; n_D^{20} 1.5143; found M 220.0; calculated M 222.23; found MR 57.34; calculated for $C_{12}H_{14}O_4$ MR 57.76.

	Found %:	C 64.27; 64.35;	H 6.44; 6.37
$C_{12}O_{14}O_4$.	Calculated %:	C 64.86;	H 6.31

c) Redistillation of Fraction IV gave 2.07 g substance which did not react with sodium and had the constants: b.p. 156-157° (11 mm); d_4^{20} 1.1071; n_D^{20} 1.4480; found M 266.7; calculated M 262.29; found MR 64.30; calculated for $C_{12}H_{22}O_6$ MR 63.08.

	Found %:	C 54.26; 54.31;	H 8.37; 8.33
$C_{12}H_{22}O_6$	Calculated %:	C 54.96;	H 8.39

The constants of the substance correspond to those of glycerol triacetal, reported in the literature [6] to have: b.p. 160-162° (14 mm); d_4^{24} 1.1067; n_D^{20} 1.4482.

Reaction of glycerol trivinyl ether with ethylene glycol in a ratio (moles) of 2:3.

34 g glycerol trivinyl ether and 18.6 g ethylene glycol were stirred together for 1/2 hour; after introduction of 1 drop (0.014 g) hydrochloric acid, the temperature rose to 91°. Fractionation of the reaction product, after neutralization with potassium carbonate, gave:

Fraction I	B.p. 74-83.5°	(760 mm);	22.67 g
Fraction II	B.p. 80-93°	(12-14 mm);	23.38 g
Fraction III	B.p. 148-149°	(4 mm);	2.50 g
Distillation residue			2.45 g

Redistillation of Fraction I gave 15.2 g (57.6% of the theoretical) of the cyclic glycol acetal (III) with the constants: b.p. 81-82°, n_D^{20} 1.4002, d_4^{20} 0.9856.

Redistillation of Fraction II failed to yield narrower cuts. The substance (21 g) collected, with b.p. 78-90° (10 mm) and n_D^{20} 1.4430, was subjected to benzoylation. No crystallization was observed on cooling the gasoline solution of the benzoylation products. Vacuum distillation yielded 20.8 g glycerol 1,2-acetal benzoate with the constants: b.p. 165-168° (12-13 mm); n_D^{20} 1.5148; d_4^{20} 1.1569.

The residue from the distillation (4.67 g) crystallized. The crystals melted at 69-70°; after many recrystallizations from a low-boiling gasoline (60-70°), 2.6 g glycol dibenzoate with m.p. 73° [7] was obtained, together with traces of the benzoate of the 1,3-acetal of glycerol with m.p. 82-83°. Literature data: m.p. 86° [6]. Fraction III, with b.p. 148-149° (4 mm); n_D^{20} 1.4762; soluble in water and reacting with metallic sodium, was glycerol.

Reaction of glycerol trivinyl ether with 1,4-butanediol in molar ratios.

21.25 g (0.125 mole) glycerol trivinyl ether and 11.25 g (0.125 mole) 1,4-butanediol were treated in conditions similar to those of the experiment with ethylene glycol. On introducing two drops (0.028 g) of HCl the temperature rose to 99°. Fractionation of the product (29.5 g), after neutralization with potassium carbonate, gave:

Fraction I	B.p. 125-128°;		5.8 g;	n_D^{20} 1.4315
Fraction II	B.p. 77-100°	(8 mm);	9.6 g;	n_D^{20} 1.4468
Fraction III	B.p. 151-156°	(10 mm);	9.25 g;	n_D^{20} 1.4505
Distillation residue			3.4 g;	n_D^{20} 1.4580

a) Fraction I was the cyclic 1,4-acetal of butanediol (XI); yield 40% of theoretical; after treatment with metallic sodium and redistillation, it had the constants: b.p. 127-128°; d_4^{20} 0.9640; n_D^{20} 1.4288; found M 117.20;

calculated M 116.15; found MR 31.33; calculated for $C_6H_{12}O_2$ MR 30.99.

	Found %:	C 62.15; 62.18; H 10.55; 10.53
$C_6H_{12}O_2$.	Calculated %:	C 62.04; H 10.41

Acetal content (by method of hydrolytic "oxylation") 98.87; 99.10% [8]

b) Fraction II, which reacted with metallic sodium, was subjected to benzoylation; the yield of benzoylation products was 10.36 g (58.2% of the theoretical), comprising 4.12 g crystalline 1,3-ethylideneglyceryl benzoate with m.p. 85° and 6.24 g liquid 1,2-ethylideneglyceryl benzoate with b.p. 157-158° (10 mm). n_D^{20} 1.5143; d_4^{20} 1.1559 [6].

c) From Fraction III, after redistillation, was isolated 5.65 g substance with b.p. 154-156° (10 mm), not reacting with sodium; its constants (d_4^{20} 1.1074; n_D^{20} 1.4483) correspond to glycerol triacetal (X) [6].

	Found %:	C 54.30; 54.26; H 8.43; 8.37
$C_{12}H_{22}O_6$.	Calculated %:	C 54.96 H 8.39

SUMMARY

1. The reaction between glycerol trivinyl ether and ethylene glycol was studied at molar and equivalent ratios (1:1 and 2:3) and between glycerol trivinyl ether and 1,4-butanediol at molar ratio (1:1).

2. Reaction between glycerol trivinyl ether and ethylene glycol and 1,4-butanediol in molar ratio leads to formation of cyclic acetals of the glycols (III) and (XI), the isomeric glycerol acetals (VIII) and (IX) and glycerol triacetal (X). Equivalent proportions of glycerol trivinyl ether and ethylene glycol yielded ethylene glycol acetal (III), glycerol 1,2-acetal (VIII) and a very minor amount of glycerol 1,3-acetal (IX).

3. The formation of cyclic acetals of glycols and glycerol is accounted for by tautomerism of the corresponding acetals.

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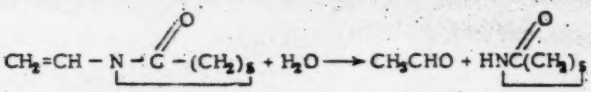
THE IONIC HYDROLYSIS OF VINYL LACTAMS IN AN ACID MEDIUM

M. F. Shostakovsky, F. P. Sidelkovskaya and M. G. Zelenskaya

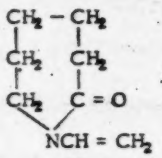
Hydration and hydrolytic cleavage constitute criteria of the reactivity of vinyl compounds. As we know, hydrolysis of a series of substances in acid and alkaline media is readily effected by an ionic mechanism. Today we know that this reaction can proceed in a neutral medium by a free-radical mechanism [1]. As was observed by Shostakovsky, a number of vinyl compounds are activated with equal ease by free-radical catalysts and by ionic catalysts. In the case of some compounds one form of activation is realized with greater facility than the other. Even in such cases, however, a suitable choice of conditions will permit reactions to be activated both by free-radical and by ionic catalysts [1].

In one of the preceding communications it was shown that vinylcaprolactam hydrolyzes under the influence of hydrogen peroxide with formation of caprolactam and acetaldehyde [2].

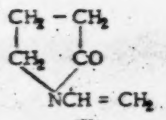


Vinyl acetate is likewise hydrolyzed under the influence of oxidizing catalysts [3]. In these cases the process takes place with a free-radical mechanism and is accompanied by polymer formation. It appeared to be of interest to investigate the ionic hydrolysis of vinyl lactams.

The present communication relates to a study of ionic hydrolysis of vinylcaprolactam (I) and vinylpyrrolidone (II) under the influence of sulfuric acid:



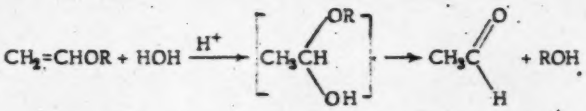
(I).



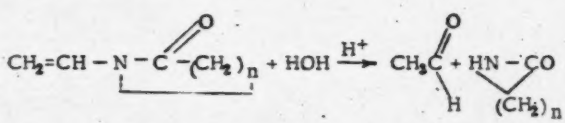
(II).

The investigated compounds were synthesized by the method of Favorsky and Shostakovsky [4].

It is known that vinylalkyl ethers with the general formula $CH_2=CHOR$ (where R is a C_1 to C_5 aliphatic radical) are readily hydrolyzed in an acid medium with formation of acetaldehyde and the corresponding alcohols. The reaction proceeds at room temperature in presence of minute amounts of acid and is extensively used for quantitative determination of vinyl ethers [5]:



In the present paper it is shown that vinyl lactams are also hydrolyzed by an ionic mechanism in presence of sulfuric acid with formation of acetaldehyde and lactams:



The process was studied in more detail with reference to vinylcaprolactam. Its hydrolysis yielded acetaldehyde and caprolactam. In working with small amounts (about 0.1 g) vinylcaprolactam, the acetaldehyde evolved was titrated with sodium bisulfite, thus permitting quantitative evaluation of the process. It was found that hydrolysis of vinylcaprolactam in a weakly acidic medium, such as approx. 0.2 N sodium bisulfite, only proceeds to the

extent of 30-35%. Addition of 2% sulfuric acid considerably accelerates the reaction, although the degree of completeness depends in large measure on the temperature. A series of experiments was carried out with the objective of developing a method of quantitative determination of vinylcaprolactam on the basis of the hydrolysis reaction. It follows from the relevant data (Table 1) that the percent hydrolysis increases with rising concentration of acid and with rise of temperature. The effect of the latter is particularly marked when working with 2% sulfuric acid. Sufficiently good and reproducible results are obtained at a temperature above 20°. On the basis of a large number of experiments it was shown that the optimum conditions for quantitative determination of vinylcaprolactam by the hydrolysis method are: employment of 2% sulfuric acid at 23-25°, and a duration of experiment of 30 minutes.

The data obtained were used for development of a method for quantitative determination of vinylpyrrolidone. It was found that in an acid medium vinylpyrrolidone is hydrolyzed with greater difficulty than is vinylcaprolactam (Table 2). In the course of the investigation it was established that the percent hydrolysis of vinylpyrrolidone increases with rising concentration of acid, with rising temperature and with the duration of the experiment. By varying these three parameters (acid concentration, temperature and time) the most satisfactory conditions for quantitative determination of vinylpyrrolidone were selected. These are: hydrolysis in a medium of 10% sulfuric acid at a temperature of 40-42° for 30 minutes.

It has thus been shown that vinylcaprolactam and vinylpyrrolidone, like vinyl ethers, are susceptible to hydrolysis by an ionic mechanism in an acid medium, vinylcaprolactam being hydrolyzed with greater facility than vinylpyrrolidone.

EXPERIMENTAL

1. Hydrolysis of vinylcaprolactam in a medium of 10% sulfuric acid. The experiment is performed in a three-necked flask fitted with mechanical stirrer, thermometer, nitrogen inlet tube, and reflux condenser connected to four Tishchenko bottles filled with distilled water (40 ml in each) for absorption of acetaldehyde. To 10.0 g vinylcaprolactam [b.p. 86.5-87° (2-2.5 mm); n_D^{20} 1.5130] is added 100 ml 10% sulfuric acid and the mixture is heated. Even at 30° the vinylcaprolactam has gone into complete solution and acetaldehyde is evolved, indicating the start of hydrolysis. The temperature of the reaction mass is then raised to 50-52° and held there for 3 1/2 hours. During this period a weak stream of nitrogen is passed though the system to facilitate removal of the acetaldehyde. The reaction product is neutralized with barium carbonate and the precipitated $BaSO_4$ is filtered off and washed five times with water. The aqueous extracts are added to the main filtrate which is then distilled, first at 16 mm (for removal of the main mass of water) and then in a higher vacuum. The final part of the distillation is carried out in a flask fitted with an ensiform side-tube. The distillation gives 5.89 g caprolactam [b.p. 119-121° (4-4.5 mm); m.p. 67.5-69°]. A mixed test with an authentic specimen of pure caprolactam does not give a melting point depression. In addition 1.79 g resin is isolated. The amount of hydrolyzed vinylcaprolactam is 72.5%. The acetaldehyde was determined in the aqueous solutions collected in the Tishchenko absorbers and in the reaction mass since the acetaldehyde could not be completely eliminated from the mass even with the help of the nitrogen stream. Determinations were effected by Ripper's method [6].

Amount of acetaldehyde found by titration:

In the Tishchenko absorbers	1.521 g
In the reaction mass	1.522 g
Total	3.043 g (calculated amount 3.16 g)

The acetaldehyde was identified as the 2,4-dinitrophenylhydrazone with m.p. 159-161° (no melting point depression in a mixed test with an authentic pure specimen).

2. Quantitative determination of vinylcaprolactam and vinylpyrrolidone. All the determinations were carried out on pure specimens which were kept for not more than 2 days after distillation. The constants of the vinylcaprolactam used were: b.p. 90.5-92° (2.5-3 mm); m.p. 34-35° The constants of the vinylpyrrolidone were: b.p. 74-74.5° (3 mm); $n_D^{19.5}$ 1.5122.

ANALYTICAL PROCEDURE

The experiments were performed in a conical flask with a ground-glass stopper and provided with special glass lugs on which were metal springs which tightly fitted the stopper into the flask. The flask was of 200-250 ml capacity. In the flask were put 20 ml sulfuric acid of known concentration and 25 ml of approx. 0.2 N sodium bisulfite solution. The flask was cooled with ice. Into the cooled mass was introduced an accurately weighed amount (60-90 mg) of the vinyl lactam, the stopper was tightly fitted and the mass was energetically shaken for

5 min, before transferring to a thermostat in which it was kept at the required temperature for the requisite period. The excess of uncombined sodium bisulfite was then titrated with 0.1 N iodine solution. A blank was run in identical conditions. The difference between the amount of iodine consumed in the blank and in the actual analysis was equivalent to the amount of hydrolyzed vinyl compound [7]. Results of complete analyses are set forth in Tables 1 and 2. Out of the large number of experiments we present the data for the most typical determinations.

TABLE 1

Conditions and results of hydrolysis of vinylcaprolactam in presence of sulfuric acid

No. of experiment	Conc. of acid in %	Hydrolysis conditions		Amount of substance found, in % of starting amount
		temperature, °C	duration, in min.	
1	2	10-12	30	62.24 58.56
2	2	23-25	30	99.40 98.20
3	10	10-12	30	96.98 95.75 95.31
4	10	23-25	30	98.86 99.12

TABLE 2

Conditions and results of hydrolysis of vinylpyrrolidone in presence of sulfuric acid

No. of experiment	Conc. of acid in %	Hydrolysis conditions		Amount of substance found, in % of starting amount
		temperature, °C	duration, in min.	
5	2	23-25	20	85.58 84.34 84.46
6	2	40-42	30	95.70 95.96
7	10	10-12	30	57.15 52.66
8	10	23-25	30	89.77 92.67 89.84
9	10	23-25	90	98.47 96.65
10	10	23-25	120	100.18 98.74
11	10	40-42	30	96.76 98.11 100.20

SUMMARY

1. It was established that vinyl lactams are hydrolyzed by an ionic mechanism in presence of sulfuric acid. It was shown, using vinylcaprolactam as starting substance, that the reaction yields lactams and acetaldehyde.

2. A procedure was elaborated for quantitative determination of vinylcaprolactam and vinylpyrrolidone. It was shown that the completeness of the determination depends upon the temperature, the duration of the experiment and the concentration of the acid used.

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THE SYNTHESIS OF CYCLOÕCTATETRAENE

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Cycloõctatetraene was first synthesized in 1911-1913 by Willstätter, Waser and Heidelberger [1, 2] by stepwise introduction of double bonds into the 8-membered carbocyclic compound obtained by decomposition of pseudopelletierine. In 1940 Reppe [3,4] obtained cycloõctatetraene from acetylene under pressure in presence of ethylene oxide and nickel cyanide. The latter investigation was the start of a series of publications by Reppe and co-workers in the period 1946-1951 on the synthesis of cycloõctatetraene. The reaction was carried out in an autoclave with intensive stirring in solution in tetrahydrofuran, in presence of complex nickel compounds and ethylene oxide or calcium carbide, under a pressure of 15-20 atm. (of which 6 atm. was created by nitrogen) and at a temperature of 60-70°. After a reaction period of 40-50 hours, cycloõctatetraene could be obtained in a yield of up to 70% of the reacted acetylene, together with other products. The latter are cuprene, benzene (10-15%), higher cyclopolyolefins [$C_{10}H_{10}$ and $C_{12}H_{12}$ (5-15%)] and a small amount of resins insoluble in tetrahydrofuran [5, 6, 7, 8, 9].

Considering the cited reaction conditions to be the optimum ones, Reppe regards tetrahydrofuran as the best solvent. The use of benzene, acetone and ether as solvents leads to lower yields of cycloõctatetraene [5, 10, 11, 12]. In discussing the effect of the type of catalyst on the results of the reaction [5, 11, 13] Reppe claims that the active catalysts are compounds of nickel in which the metal is combined in the form of a complex in a very labile condition, for example nickel cyanide, nickel acetylacetonate, nickel ethyl acetate, nickel oxalylbenzoylterephthaloyl and nickel orthoaminophenol [5, 7, 10, 14].

The employment as catalysts of nickel chloride or nickel bromide, in which the nickel is firmly combined with halogens by an ionic bond, or of nickel terephthalocyanine (a complex compound but with the nickel in firm combination), proved to be unsuitable for the purpose [5]. The use has been reported as catalysts, however, of nickel halides together with ethylene oxide [14], as well as of copper compounds [15]. During the synthesis nitrogen is used as a diluent of the acetylene to prevent possible decomposition of the latter (risk of explosion in the drastic conditions of the reaction) [9, 10, 13].

The employment for cycloõctatetraene synthesis of pressures of the order of 30 atm., i.e. nearly double those recommended by Reppe, is reported in a paper by Raymond [16]. In another publication [17], reviewing Reppe's work, reference is made to Reppe's use of temperatures of 70-150° and pressures of 15-20 atm, although the yield of cycloõctatetraene is not stated (data are also lacking on this point in Reppe's original papers). An earlier paper [18] also refers to the use of high temperatures (70-100°) during the synthesis of cycloõctatetraene from acetylene under pressure. There are indications that the yield of cycloõctatetraene in these conditions is fairly low (36% of the converted acetylene). The other products of the reaction are: benzene, 6%; cuprene, 12%; and resins, 36%. These results are substantially in agreement with those of Cope [19]. In the latter investigation, in which the author followed the reaction conditions recommended by Reppe (temperature of 90°), the yield of cycloõctatetraene was about 50% of the acetylene consumed.

Problems of the synthesis of cycloõctatetraene from acetylene under pressure by a catalytic method are also discussed in a number of papers of a review character. The information given in these papers is mainly a repetition of the material discussed above. It is perfectly obvious that many of the conclusions and suggested possibilities of of synthesis contained in these papers are to some extent exaggerated [20]. In addition to studies concerned with the synthesis of cycloõctatetraene from acetylene under pressure, papers have appeared on the preparation of cycloõctatetraene by other methods. Thus, Cope and Overberger [21] synthesized cycloõctatetraene from pseudopelletierine. These synetheses are lacking in originality since the methods employed are already known from the synthesis of Willstätter. In another paper [22] a method is described for the preparation of cycloõctatetraene from an 8-membered cyclic dimer of chloroprene.

The mechanism of formation of cycloõctatetraene from acetylene has been inadequately studied. Reppe [5, 10, 11, 13] thinks that the role of the active catalyst is played by labile acetylenic compounds (not isolated in the free state); their formation is promoted by the presence of cyclic oxides (ethylene oxide and tetrahydrofuran). Bergman [23] criticizes Reppe's theory and suggests that the acetylene first dimerizes to vinylacetylene which further dimerizes to cyclic compounds. An entirely different theory is expounded by McKinley [24] who considers

that cyclooctatetraene is formed via complex compounds of nickel with tetrahydrofuran. There is no agreed theory about the mechanism of formation of cyclooctatetraene.

An analysis of the literature data on the synthesis of cyclooctatetraene leads to the following conclusions: a) the synethsis of cyclooctatetraene by the usual recipes and methods of classical organic chemistry is extremely complicated and of little interest for technical purposes; b) the new and highly productive method of synthesis by catalytic polymerization of acetylene under pressure possesses considerable advantages; c) the latter reaction has remined practically without study and trustworthy theories of its mechanism are lacking. Agreement is also lacking as to the optimum temperature of the reaction and the optimum pressure range; the function of various reaction components and the necessity for their introduction have not been established, and so on.

EXPERIMENTAL

The purpose of our research was the examination of the influence of various factors on the course of the polymerization of acetylene with the aim of obtaining maximum yields of cyclooctatetraene when starting from industrial acetylene. A study was made of the influence of the following factors on the yield and rate of formation of cyclooctatetraene during catalytic polymerization of acetylene under pressure: 1) the nature of the solvent for the acetylene; 2) the nature of the catalyst; 3) the amount of catalyst; 4) the content and amount of the acetylene diluent; 5) the type of dehydrating agents; 6) the presence in the sphere of reaction of water and other impurities; 7) the reaction temperature; 8) the method of catalysis; 9) the magnitude of the acetylene pressure.

All the starting materials were subjected immediately prior to their use to careful purification and were characterized by the appropriate method.

The dioxan was distilled over KOH to remove peroxides and then fractionally distilled over sodium to remove traces of moisture. After distillation it had the constants: b.p. 100.4-100.8° (760 mm); n_D^{20} 1.4222 ± 0.0001.

Tetrahydrofuran was purified by the same procedure as for dioxane and had the constants: b.p. 64.5-64.8° (760 mm); n_D^{20} 1.4089 ± 0.0001. The benzene was a cryoscopic grade and was distilled over sodium. After distillation it had the constants: b.p. 80.1° (760 mm); n_D^{20} 1.5017 ± 0.0001. Tetralin was distilled under reduced pressure: b.p. 110° (40 mm); n_D^{20} 1.5402 ± 0.0001. Acetone was purified, dried and distilled, after which it had b.p. 55.5-56.8° (760 mm). Ethylene oxide was distilled over sodium and then had b.p. 10.9-11.2° (760 mm). CaC_2 was specification (GOST)* material. The silica gel was dehydrated by heating at 110° for 8 hours. The $CoCl_2$ was analytical-grade material. The phthalic anhydride was pure for analysis. The aluminum acetylacetonate was subjected to recrystallization. The nickel acetylacetonate was sublimed and then had m.p. 218°. Nickel cyanide was tested for absence of Cl ion. The nitrogen was technical material with up to 2% O_2. The acetylene was standard (GOST) grade.

Catalytic Polymerization of Acetylene under Pressure

The reaction vessel was a vertical autoclave of V4A steel, designed for a maximum working pressure of 200 atm at 500° (working capacity 1 liter). Energetic stirring of the reaction mixture was effected with a stirrer of the rotor type reaching nearly to the bottom of the autoclave and running at 250-300 r.p.m. The temperature in the autoclave was measured with a mercury thermometer and was kept constant to ± 2°, using a cylindrical furnace whose electrical heating was regulated with a rheostat. Experiments were run in the following manner: With the cover removed, the autoclave was charged with the solid and liquid starting materials; the cover was then replaced, the stirrer was started and the tightness of the closure was tested by passing a stream of nitrogen for 30 min. and observing whether the pressure was maintained for 10 to 15 minutes. When this test was completed, the nitrogen was discharged from the autoclave and a stream of acetylene was passed through for 2-3 min. until the oxygen content of the exit gas was not more than 0.5% (the residual pressure was 1.5 atm.) The autoclave was then heated to the required reaction temperature and acetylene was fed in directly from a cylinder until attainment of the requisite pressure. During the reaction the working pressure was regulated by one of the following three methods: 1) Periodic addition of acetylene from the cylinder to offset the fall in pressure due to the reaction; 2) feeding of a constant stream of acetylene from the cylinder during the reaction period; 3) development in the autoclave of a pressure exceeding that in the cylinder (when carrying out the reaction in the absence of a diluent by raising the temperature in the autoclave containing the acetylene dissolved at room temperature. Before each addition of acetylene, samples of the liquid and gas phases were withdrawn. The gas samples were analyzed qualitatively and quantitatively for the following substances: CO_2, to obtain information about the oxidation reactions; R—CHO, to establish the presence of water, unsaturated compounds of the type of vinylacetylene, to gain an insight into the intermediate stages of the reaction; oxygen, to elucidate its influence on the course of the reaction (cuprenization). The liquid phase

* All-Union State Standard.

samples were filtered and the refractive index of the filtrate was determined to an accuracy of 0.0001. The amount of acetylene consumed was calculated with allowance for the free space in the autoclave and for the physical parameters (T and p) and was checked by weighing the autoclave before and after the reaction. The reaction was stopped when the refractive index had reached its maximum (n_D^{20} 1.475 - 1.480 in the case of dioxan) and the pressure had ceased to drop. The reaction products were withdrawn from the autoclave and filtered through a Buchner funnel to separate the cuprene formed during the reaction. Adsorbed liquid products of reaction were extracted from the cuprene in a Soxhlet and the filtrate was rectified under reduced pressure in a nitrogen stream in presence of an inhibitor (hydroquinone). The rectification yielded the following fractions: 1) Solvent – up to 60°; 2) cyclooctatetraene – 60.9° (46.5 mm); 3) still residue: a) yellow liquid with b.p. 96° (5 mm); b) blue liquid, b.p. 135° (5 mm); c) resins insoluble in tetrahydrofuran or in dioxan. The extract from the cuprene was similarly rectified. The rate of rectification was adjusted to enable the cyclooctatetraene to be obtained free from any impurities whatsoever (as verified by the b.p. in vacuum, the n_D^{20} and n_D^{25}).

As a safeguard against oxidation, the cyclooctatetraene isolated in the process was sealed into ampoules under vacuum or in a nitrogen stream; the ampoules were of 50-100 ml capacity and were kept in the dark at 20°. Of the products of the reaction, the cyclooctatetraene was the one subjected to more thorough investigation, while the cuprene was examined less closely. The results of examination of the remaining products of reaction are not considered in this paper.

Influence of nature of solvent on the rate of polymerization of C_2H_2 and the yield of cyclooctatetraene.

The solvents studied in this connection were tetrahydrofuran, dioxan, benzene, tetralin and acetone. All the experiments in which these substances were used as solvents were performed in the following constant conditions: 1) Reaction temperature 85 ± 2°; 2) C_2H_2 pressure 28-12 atm; 3) amount of catalyst 0.6 g calculated on the cation; 4) amount of solvent 100 g; 5) duration of reaction 20 hours; 6) free oxygen content of the autoclave in accordance with GOST limit for C_2H_2 (0.3%). The speed of polymerization was expressed as the number of grams of acetylene polymerized per hour, taking a mean value based on the total reaction period of 20 hours. (The curves in Fig. 1 show the reaction rate at various periods throughout the process.) The results of the experiments are set forth in Tables 1 and 2.

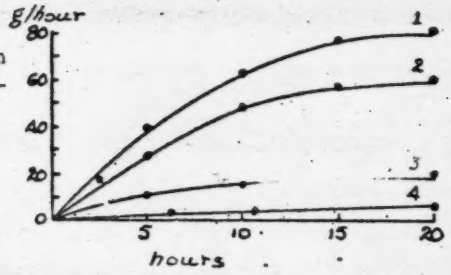

Fig. 1. Dependence of the rate of polymerization of C_2H_2 on the nature of the solvent: 1-dioxan; 2- tetrahydrofuran; 3-benzene; 4- tetralin

Influence of the nature of the catalyst on the reaction rate and the yield of cyclooctatetraene. Catalysts tested in this connection were nickel cyanide, cobalt chloride, aluminum acetylacetonate and nickel acetylacetonate. All the experiments using these catalysts were performed with maintenance of the same constant conditions as in the preceding experiments. The results of the experiments are set forth in Tables 3 and 4 and plotted in Figs. 2 and 3.

Influence of the amount of catalyst on the rate of polymerization of C_2H_2 and on the yield of cyclooctatetraene. Experiments were carried out in the indicated conditions (but with 250 g solvent) with the following amounts of additives: nickel acetylacetonate 15, 7.5 and 3.2 g; nickel cyanide 10 and 3.2 g. Results of the experiments are set forth in Table 5 and plotted in Fig. 4.

Influence of diluent on the rate of polymerization of C_2H_2 and on the yield of cyclooctatetraene. For clarification of the influence of a gaseous, inert diluent on the rate of polymerization under pressure and on the yield of cyclooctatetraene, nitrogen containing 2% oxygen (Orsat determination) was used. All the experiments were performed with maintenance of the following condition: temperature 85 ± 2°, C_2H_2 pressure 28-12 atm.; amount of solvent (tetrahydrofuran) 250 g, amount of ethylene oxide 16 g; total duration of reaction

20 hours; amount of catalyst 0.6 g (calculated on the cation). Results are set forth in Table 6 and plotted in Fig. 5.

TABLE 1

Dependence of the rate of polymerization and yield of cyclooctatetraene on the nature of the solvent when using nickel acetylacetonate as catalyst

Number of experiments	Solvent	Number of grams C_2H_2 per hour	Yield in %		
			C_8H_8	cuprene	remaining* products
3	Dioxan	4.0	72	10	18
2	Tetrahydrofuran	3.0	45	32	23
2	Benzene	1.0	30	30	40
2	Tetralin	0.6	25	25	50

* These are taken to comprise the volatile products of the first fraction, the residue in the still, and losses.

TABLE 2

Dependence of the rate of polymerization and yield of cyclooctatetraene on the nature of the solvent when using nickel cyanide as catalyst

Number of experiments	Solvent	Number of grams C_2H_2 per hour	Yield in %		
			C_8H_8	cuprene	remaining products
2	Dioxan	3.0	68	14	18
3	Tetrahydrofuran	2.0	45	30	25
2	Benzene	0.8	32	30	38
2	Tetralin	0.5	20	25	55

TABLE 3

Dependence of the rate of polymerization of C_2H_2 and the yield of cyclooctatetraene on the nature of the catalyst when using dioxan as solvent

Number of experiments	Catalyst	Amount, in g	No. of g C_2H_2 per hour	Yield in %		
				C_8H_8	cuprene	remaining products
3	Nickel acetylacetonate	3.2	4.0	72	10	18
2	Nickel cyanide	1.5	3.0	68	14	18
2	Aluminum acetylacetonate	1.0	0	0	0	0
2	Cobalt chloride	1.7	0	0	0	0

TABLE 4

Dependence of the rate of polymerization of C_2H_2 and the yield of cyclooctatetraene on the nature of the catalyst when using tetrahydrofuran as solvent

Number of experiments	Catalyst	Amount, in g	No. of g C_2H_2 per hour	Yield in %		
				C_8H_8	cuprene	remaining products
2	Nickel acetylacetonate	3.2	3.0	45	32	23
3	Nickel cyanide	1.5	2.0	45	30	25
2	Aluminum acetylacetonate	1.0	0	0	0	0
2	Cobalt chloride	1.7	0	0	0	0

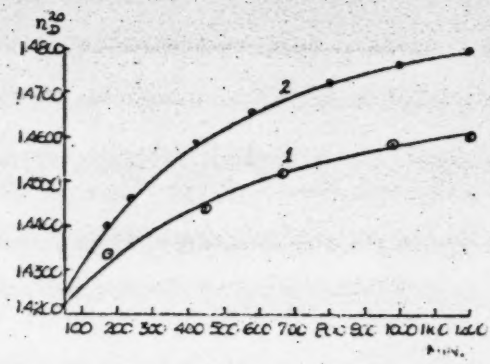

Fig. 2. Dependence of rate of polymerization on the nature of the catalyst (solvent dioxan): 1) nickel cyanide, 2) nickel acetylacetonate

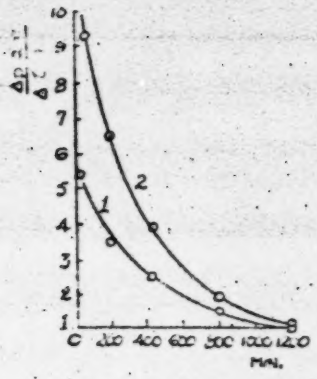

Fig. 3. Dependence of the rate of polymerization of C_2H_2 on the nature of the catalyst (solvent tetrahydrofuran): 1) nickel cyanide; 2) nickel acetylacetonate

TABLE 5

Dependence of velocity of polymerization of C_2H_2 and the yield of cyclooctatetraene on the amount of catalyst when using dioxan as solvent

Number of experiments	Catalyst	Amount, in g	No. of g C_2H_2 per hour	Yield in %		
				C_8H_8	of cuprene	of remaining products
2	Nickel acetylacetonate	15	12.6	38	27	35
2	Nickel acetylacetonate	7.5	10.5	58	17	25
6	Nickel acetylacetonate	3.2	9.5	70	10	20
2	Nickel cyanide	10	9	45	35	20
5	Nickel cyanide	3.2	8.2	70	12	18

TABLE 6

Dependence of rate of polymerization of C_2H_2 and of yield of cyclooctatetraene upon the diluent when using nickel cyanide as catalyst

Number of experiments	Diluent	Amount, in %	No. of g C_2H_2 per hour	Yield in %		
				C_8H_8	of cuprene	of remaining products
2	Nitrogen	0	8.80	45	30	25
2	Nitrogen	10	6.0	43	28	29
3	Nitrogen	30	3	45	27	30
2	Nitrogen	50	2	45	32	23

Influence of nature of dehydrating media on the rate of polymerization of C_2H_2 and on the yield of cyclooctatetraene. The following compounds were studied: ethylene oxide, calcium carbide, silica gel, and phthalic anhydride. The dehydrating agents were introduced in the amount of 6% calculated on the solvent. The amount of solvent was 100 g. The remaining reaction conditions were the same as in the preceding experiments. Results are set forth in Tables 7 and 8. Silica gel and phthalic anhydride had no appreciable influence upon the reaction course.

Influence of water and other impurities on the rate of polymerization of C_2H_2 and on the yield of cyclooctatetraene. The qualitative effect of water and other impurities on the rate of polymerization of C_2H_2 was studied in all the experiments while maintaining constant conditions with introduction of 250 g solvent. The results of these experiments are set forth in Table 9.

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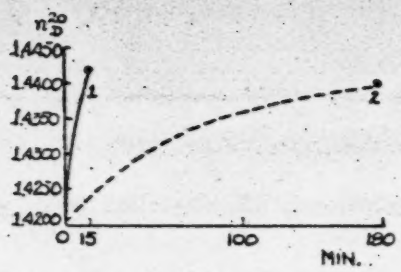

Fig. 6. Influence of poor heat transfer on the rate of polymerization of C_2H_2: 1) poor heat transfer (in 15 min. the temperature rose from 85 to 150°) 2) normal withdrawal of heat (temperature of 85° did not change)

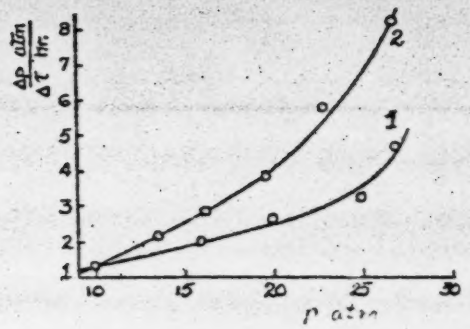

Fig. 7. Dependence of rate of polymerization of C_2H_2 on the pressure at 85°: 1) nickel cyanide; 2) nickel acetylacetonate

TABLE 9

Dependence of rate of polymerization of C_2H_2 and the yield of cyclooctatetraene on the presence of impurities

Number of experiments	Water or other impurities	Solvent	Catalyst	Grams of C_2H_2 per hour	Yield of C_8H_8, in %
2	Water	Tetrahydrofuran	Nickel cyanide	0	0
2	Non-dehydrated solvent	Dioxan	Nickel cyanide	6.7	55
2	Undistilled solvent	Dioxan	Nickel cyanide	5.7	50
2	Air dry catalyst	Dioxan	Nickel acetyl-acetonate	2.7	45

TABLE 10

Dependence of rate of polymerization of C_2H_2 and yield of cyclooctatetraene on the thermal regime when using nickel cyanide as catalyst

Number of experiments	Temperature in °C	Grams of C_2H_2 per hour	Yield, in %		
			C_8H_8	of cuprene	of remaining products
3	95-116	13	35	40	25
3	90-95	10	40	35	25
4	85	8.8	43	30	27
3	75	5	45	32	23
2	65	3	48	25	27

TABLE 11

Dependence of rate of polymerization of C_2H_2 on the pressure

Nickel acetylacetonate			Nickel cyanide		
Number of experiments	Pressure in atm.	$\Delta P/\Delta t$ at 85°	Number of experiments	Pressure in atm.	$\Delta P/\Delta t$ at 85°
5	27	8.10	4	27	4.60
3	23	5.77	3	23	3.0
4	19.7	3.80	4	19.7	2.45
4	16.3	2.15	3	16.3	2.0
3	13.6	2.15	3	13.6	1.40
3	10	1.40	3	10.0	1.30

Influence of reaction temperature on the rate of polymerization of C_2H_2 and on the yield of cyclooctatetraene. All the experiments for study of the temperature effect were performed in tetrahydrofuran (250 g) with introduction of ethylene oxide (6%). Results are set forth in Table 10 and plotted in Fig. 6.

Influence of pressure on the rate of polymerization of C_2H_2. In experiments for clarification of the influence of the pressure, the solvent used was dioxane (250 g) in otherwise identical conditions. Results of the experiments are set forth in Table 11 and plotted in Fig. 7.

Results of analysis of the reaction products. Fully identical results were obtained in all the above experiments; the following constants were found, for example, for cyclooctatetraene:

Our data	Reppe's data
B.p. 60° (46.5 mm); n_D^{20} 1.5342;	B.p. 60° (46.79 mm); n_D^{20} 1.5290;
M.p. 6.5; mol. wt. 103.4; d_4^{20} 0.9200	M.p. 7°; mol. wt. 103.5; d_4^{20} 0.9206.

Data for analysis of cyclooctatetraene:

Found %: C 92.25; H 7.98
Calculated %: C 92.30; H 7.70

Data for analysis of cuprene:

Found %: C 62.51; H 6.63; ash 28.41

Neither in the cold nor after prolonged extraction whilst heating did cuprene go into solution in any of the common organic solvents or in dilute and concentrated inorganic acids.

EVALUATION OF RESULTS

As already mentioned, the aim of the present paper was to study the synthesis of cyclooctatetraene by catalytic polymerization of acetylene under pressure for the purpose of characterization of the influence on the course of the reaction and on the yield of cyclooctatetraene of the main physicochemical factors. Since in none of the previously published literature is there a characterization of the principal raw material employed (acetylene) or any mention of the purification of acetylene under pressure, we used technical acetylene which proved to be suitable for this reaction. Our attempts to reproduce the synthesis of cyclooctatetraene by the procedure described by Reppe did not give satisfactory results. This led us to doubt the expediency of making use in the investigation of many of the basic data published in the literature as a basis of the investigation.

The solvents used in an examination of the influence of different solvents on the course of the reaction were dioxan, tetrahydrofuran, benzene, tetralin and acetone. Tetrahydrofuran was included in the tests because it was necessary to check the literature data according to which tetrahydrofuran is the best solvent for the process in question. Benzene was used as a representative of the aromatic hydrocarbons. During the investigation, the literature data were confirmed according to which tetrahydrofuran is a better solvent for this process than benzene, acetone or tetralin, but the claims that it was the best solvent in general were refuted, since the best synthesis results both in regard to the reaction velocity and to the yield of cyclooctatetraene were attained when using (for the first time in this reaction) dioxan as the solvent, as clearly shown by Fig. 1.

Consequently the intensification of the effect of the functional groups of the cyclic ether led to intensification of the reaction. The more pronounced hydrocarbon character of the solvent resulting from replacement of tetralin by benzene led to diminution of the activity of the reaction course. Employment of a catalyst soluble in the liquid phase (in the case of homogeneous catalysis) appreciably intensifies the reaction. Consequently nickel acetylacetonate slows down the higher velocity of the reaction without substantially reducing the yield of product. It should be noted that the literature reports in all cases recommend the use of nickel cyanide but evidently without realizing the implications of the foregoing observations. Apart from the nickel catalysts mentioned above, we also tested a few other compounds. To test the possibility of using as catalysts elements in the same group of the periodic system as nickel i.e. possessing a similar electronic configuration, $CoCl_2$ was used. In experiments with the latter, however, not even traces of cyclooctatetraene were obtained nor, in general, any signs of reaction of acetylene at all.

Experiments with another compound – aluminum acetylacetonate – as catalyst were performed with the aim of testing the influence of the anionic component of a catalyst on the course of the reaction. Substitution of nickel by aluminum, however, in nickel acetylacetonate – the best of all the catalysts studied – leads to complete disappearance of the catalytic action. This fact appears to us to be evidence that the anion does not play any independent catalytic role in this reaction. The intensification of the catalytic activity when nickel acetylacetonate is substituted for nickel cyanide is evidently due to a change in the character of the catalysis (homogeneous in the latter case and heterogeneous in the former). Thus the creation of conditions of homogeneous catalysis is preferable and permits a considerable reduction of the duration of reaction. Concerning, on the other hand, the amount of catalyst, its

effect is developed in the following manner: Both in the case of heterogeneous catalysis (nickel cyanide) and of homogeneous catalysis (nickel acetylacetonate), an increase in the amount of catalyst (using the same amount of solvent) causes the reaction velocity to increase, but at the same time the yield of cyclooctatetraene is lowered. It is characteristic that when using nickel acetylacetonate the increase in the amount of catalyst brings about a drop in yield of cyclooctatetraene which is associated with increased yields of both cuprene and the remaining products, whereas when using nickel cyanide the reduced cyclooctatetraene yield is bound up in the main with higher yields of cuprene only. On the basis of comparison of the results of the individual experiments we can recommend optimum ratios of solvent and catalyst which will guarantee an adequate yield at a satisfactory reaction velocity. Addition of nitrogen considerably lowers the reaction velocity. Our numerous experiments showed that the process is perfectly free from hazards even when using undiluted acetylene if our safety procedure is strictly observed.

New data that we have obtained, especially when working in the absence of a diluent, vividly demonstrate that the application of all the conditions of synthesis used by other investigators is by no means essential. These data even showed the opposite: certain factors of synthesis described in the literature prove to have a negative influence on the course of the process. This fact is even more strikingly manifested by a critical evaluation and check of the need for using such completely necessary (in Reppe's opinion) reaction components as ethylene oxide and calcium carbide. It was actually found that the omission of these compounds during the synthesis affords the possibility of obtaining higher yields of cyclooctatetraene at a relatively small decrease of reaction velocity. Consequently neither ethylene oxide nor calcium carbide are indispensable components of the reaction and their interchangeability is the possible result of their greater or lesser inertness in respect of the reaction. In the light of these facts the assertion of Reppe that ethylene oxide plays a decisive part in the mechanism of formation of cyclooctatetraene does not bear criticism.

The purity and dryness of the starting materials play an important part in the polymerization of acetylene to cyclooctatetraene under pressure. Water completely inhibits the reactions. Use of undried starting materials shows down the reaction and leads to reduced yields. Impurities in the catalyst have a similar effect and thorough purification is therefore necessary.

The high exothermal effect of the reaction makes absolutely essential the strict maintenance of the correct temperature regime and of the conditions for normal heat removal. A rise of temperature to 85° has no appreciable effect on the yield but leads to a considerable increase of reaction rate. The yield of cyclooctatetraene only falls markedly when the temperature rises above 85°. Thus the optimum temperature ensuring a sufficiently high reaction rate in association with maximum yield of cyclooctatetraene is about 85°. A rise of the initial pressure exerts a similar influence on the reaction rate to that of temperature rise. A threefold increase of the pressure leads to an approximately 3 ½ - fold increase in the velocity of the homogeneous catalytic reaction. In that case, however, the increased rate does not lower the yield. It is consequently expedient to conduct the process at a constant pressure of the order of 25-28 atm, which necessitates a constant flow of acetylene into the reaction vessel. The production during the polymerization of acetylene of any particular compound as main product, in a substantial yield, is governed by the choice of such conditions of performance of the reaction and of bringing together of the reaction components as will ensure that the required direction of the reaction becomes the predominant one while all the other directions are inhibited to the maximum extent. The occurrence of side reactions in our experiments led to the appearance in greater or lesser degree of the following in the reaction product: cyclooctatetraene, cuprene, benzene, styrene, a yellow product of unknown structure, with b.p. 96° (5 mm), a blue product of unknown structure with b.p. 135° (5 mm) and several other more volatile or higher molecular compounds. According to the literature data, the same process, but in somewhat different conditions, led to formation of higher cyclopolyolefins.

These diverse directions of the process are the result of the effect of a large number of factors. There are, however, two main competing directions of the reaction: the formation of cyclooctatetraene and the formation of cuprene, and these have also been studied in our research. If it were possible to regulate the process to yield only these two products, the problem could be regarded as substantially solved, for the amount of all the remaining products of the reaction is relatively small. But the mastery of even these two directions of the reaction is quite a difficult problem, and even though our investigation has shown that it is possible in practice to conduct the process in the required direction, the theoretical aspects of the problem remain unclarified. The greatest difficulties in the theoretical investigation of the characteristics of the process arise when we consider the mechanism of the reaction.

Our experimental data refute the mechanism proposed by Reppe which involved formation of an active catalyst (nickel acetylide), starting from the presence of ethylene oxide in the sphere of reaction, since it was shown that the reaction also proceeds in the absence of ethylene oxide. Any other more acceptable mechanism of the reaction has not yet been advanced.

SUMMARY

1. The polymerization of acetylene under pressure in presence of catalysts proceeds with formation of various compounds. The particular direction followed by the reaction, and consequently also the yield of cyclooctatetraene, depends on the reaction conditions (nature of solvent, catalyst, temperature, pressure, presence of additives, etc.)

2. The type of catalysis plays an important part in regard to the course of the process, especially in connection with the reaction velocity. The homogeneous catalysis which we carried out has substantial advantages over heterogeneous catalysis as used by Reppe.

3. A non-hazardous course of the reaction can be achieved without resorting to special dilutions of the acetylene (e.g. with nitrogen), by conducting the reaction in presence of the vapor of those liquids which enable precise maintenance of the reaction regime.

4. Technical acetylene may be used both for the practical production of cyclooctatetraene and for investigation of the main characteristics of the process.

5. In a series of studies of solvents, the best results are got with dioxan (used by us for the first time for this reaction) which has definite advantages over the best of the solvents described in the literature (tetrahydrofuran), particularly in respect of reaction velocity.

6. Nickel acetylacetonate, which acts homogeneously in a dioxan medium, is a more active catalyst than nickel cyanide. The activity of the catalyst (in the heterogeneous process) decreases due to additional cuprene formation and deposition of carbon black.

The process of cuprenization is intensified with increasing amount of catalyst in presence of ethylene oxide and calcium carbide, also on rise of temperature to 90-100°. The poor heat conduction combined with the strong exothermicity of the process leads to a marked temperature rise and to nearly complete transformation of the acetylene into cuprene. The optimum reaction temperature is between 82 and 87°.

7. The polymerization of acetylene to cyclooctatetraene proceeds in the absence of ethylene oxide and calcium carbide. Introduction of the latter compounds is not only unnecessary but is even detrimental to the process (slight reduction in the yield of cyclooctatetraene).

8. Inhibitors of the reaction are traces of water and impurities (of undetermined chemical structure) present in the catalyst.

9. The yield of cyclooctatetraene increases with increasing pressure in the reaction space.

10. A yield of over 70% cyclooctatetraene is attained with good reproducibility of individual experiments and high reaction velocity.

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ORGANOSILYL ESTERS OF ACETIC AND ISOBUTYRIC ACIDS

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Organosilyl esters of the general formula $R_3SiOOCR'$ have received only cursory study. Descriptions have been published of only four esters of acetic acid containing, as the radical R, methyl [1, 2, 3], ethyl [4], n-propyl [5] or phenyl [6, 7] groups, and of only one each of the esters of butyric, isovaleric and enanthic acids in which R was the ethyl radical [8]. Complex organosilicon esters of the general formula $R_2R''SiOOCR'$ have not previously been described. In this paper we present the properties of four esters, synthesized for the first time, of acetic and isobutyric acids of the type of $R_2R''SiOOCR'$ and $R_3SiOOCR'$.

All the esters were prepared by reaction of anhydrous sodium acetate or isobutyrate with R_3SiCl or $R_2R''SiCl$ by heating for 10-15 hours in a medium of dry ligroine at 60-85° with energetic stirring. After separating the precipitated NaCl and the excess of organic acid salt, the ester was isolated in the pure form by repeated vacuum fractionation in a current of dry air. All the prepared esters were transparent, colorless, easily hydrolyzed (by water) liquids of faint odor. The starting R_3SiCl and $R_2R''SiCl$ were obtained by the action of RMgBr on $SiCl_4$ or methylchlorosilane. $(C_4H_9)_3SiCl$ was prepared by the action of n-C_4H_9MgBr on $SiCl_4$ and was isolated in the pure form by decomposition of the butylsiloxanes with freshly sublimed $AlCl_3$ [9]. $CH_3(C_4H_9)_2SiCl$ was prepared by a similar method: action of n-C_4H_9MgBr on CH_3SiCl_3. Symmetrical dimethyltetra-n-butyldisiloxane was obtained as intermediate product.

Silicon was determined by ashing a weighed amount of substance with a mixture of conc. HNO_3 and H_2SO_4; chlorine by direct titration with 0.1 N NaOH in presence of phenolphthalein; the ester number by saponification with KOH solution in diethylene glycol [10]; the molecular refraction was calculated by Warrick's method [11].

EXPERIMENTAL

Methyldi-n-butylsilyl acetate $CH_3(C_4H_9)_2SiOOCCH_3$ was prepared from 45 g (0.23 mole) $CH_3(C_4H_9)_2SiCl$ and 30 g (0.37 mole) CH_3COONa. Yield about 70%; b.p. 83° (8 mm); n_D^{20} 1.4284; d_4^{20} 0.8568; found M 206; calculated M 216.3; found MR 65.0; calculated MR 63.45. found ester number 261,267; calculated 259.2.

Found %: Si 12.52; 13.2

$C_{11}H_{24}O_2Si$. Calculated %: Si 12.96

Methyldi-n-butylsilyl isobutyrate $CH_3(C_4H_9)_2SiOOCCH(CH_3)_2$ was prepared from 30.5 g (0.2 mole) $CH_3(C_4H_9)_2SiCl$ and 33.2 g (0.3 mole) $(CH_3)_2CHCOONa$. Yield about 60%; b.p. 105-107° (5 mm); 134-140° (20 mm); n_D^{20} 1.4238; d_4^{20} 0.8620; found mol. wt. 249, calc. 244.4; found MR 72.32; calculated MR 72.71; found ester number 218; calculated 229.5.

Found %: Si 10.77

$C_{13}H_{28}O_2Si$. Calculated %: Si 11.47

Tri-n-butylsilyl isobutyrate $(C_4H_9)_3SiOOCCH(CH_3)_2$ was prepared from 25 g (0.1 mole) $(C_4H_9)_3SiCl$ and 25 g (0.22 mole) $(CH_3)_2CHCOONa$. Yield 61%; b.p. 145-146° (13 mm); 160° (20 mm), n_D^{20} 1.4345; d_4^{20} 0.8663; found molecular weight 280.8; 291; calculated 286.5; found MR 86.21; calculated MR 86.60; found ester number 199.3; 205.8; calculated 202.9.

Found %: Si 9.38; 9.55

$C_{16}H_{34}O_2Si$. Calculated %: Si 9.79

Dimethylphenylsilyl isobutyrate $(CH_3)_2C_6H_5SiOOCCH(CH_3)_2$ was prepared from 20 g (0.11 mole) $(CH_3)_2C_6H_5SiCl$ and 25 g (0.22 mole) $(CH_3)_2CHCO \cdot ONa$. Yield of pure ester 10%; b.p. 114-116° (6 mm); n_D^{20} 1.4909; d_4^{20} 0.9844; found mol. wt. 215; 218; calculated 222.3; found MR 65.4; calculated MR 64.75; found ester number 249; calculated 252.3.

Found %: Si 12.1; 12.28

$C_{12}H_{18}O_2Si$. Calculated %: Si 12.62

Methyl-n-butylchlorosilane $CH_3(C_4H_9)_2SiCl$ was prepared from $n\text{-}C_4H_9MgBr$ and CH_2SiCl_2 in the ratio of 2:1; b.p. 193-198°; n_D^{20} 1.4325; d_4^{20} 0.8656; found MR 57.73; calculated MR 58.0.

	Found %:	Cl 18.3
$C_9H_{21}SiCl$.	Calculated %:	Cl 18.45

Symmetrical dimethyltetra-n-butyldisiloxane $[CH_3(C_4H_9)_2Si]_2O$ was isolated from the products of hydrolysis and dehydration of methyl-n-butylchlorosilane (V). B.p. 150-152° (5 mm); n_D^{20} 1.4336; d_4^{20} 0.8281; found mol. wt. 345; 347; calculated 330.6; found MR 103.7; calculated MR 104.48.

	Found %:	Si 16.98; 17.1
$C_{16}H_{38}OSi_2$.	Calculated %:	Si 16.95

SUMMARY

1. The following 4 new organosilyl esters were synthesized by reaction of the Na salts of acetic and isobutyric acids with alkylchlorosilanes: methyldi-n-butylsilyl acetate; methyldi-n-butylsilyl isobutyrate; tri-n-butylsilyl isobutyrate; and dimethyldiphenylsilyl isobutyrate.

2. Intermediate compounds obtained were the previously undescribed methyldi-n-butylchlorosilane and symmetrical dimethyltetra-n-butyldisiloxane.

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THE OPTICAL METHOD OF INVESTIGATION OF HYDROCARBONS

COMMUNICATION 7. RAMAN SPECTRA OF SOME NAPHTHENES

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The present investigation is one of a series on the scattering spectra of pure hydrocarbons systematically carried out in the laboratories of the Institute of Physics and the Institute of Organic Chemistry of the Academy of Sciences of the USSR since 1939 [1-6].

The hydrocarbons hitherto examined were mainly those boiling within the range of 28 and 130° and whose Raman spectra can already serve as a basis for analysis of the individual composition of the most important fractions of straight-run gasolines. The list of investigated hydrocarbons presenting interest from the view point of analysis of gasolines in the indicated temperature range is, however, still incomplete: up to now we have studied all the liquid paraffinic hydrocarbons containing 5 to 8 carbon atoms and some of the nonanes, while of the naphthenes we have only studied those most frequently encountered in petroleums. In the present paper we set forth data for another seven naphthenes which are difficult to synthesize and which have boiling points between 108 and 142°.

In previous communications [1-5] exploratory spectral data were submitted for a series of hydrocarbons which for one reason or another were insufficiently pure. Subsequently a considerable number of these hydrocarbons were synthesized afresh and purified more thoroughly. Starting with the present communication, we shall set forth data about changes which ought to be made in previously published results. Thus, in the present paper we give details of spectra of freshly synthesized and extremely pure trans-1,4-dimethylcyclohexane, which supersede the earlier data for this preparation based on material containing an appreciable amount of the cis-form; in addition we publish new data for the spectra of newly synthesized n-octane and 2,5-dimethylhexane.

The apparatus and experimental procedure were described in previous communications [1,2,3]. The intensities of the spectral lines at the maxima were determined by the method of photographic photometry. Since all results were obtained in identical conditions, the new data are comparable with those previously published.

RESULTS OF MEASUREMENTS

Below we present the results of studies of the frequency and intensity of the spectra of eight naphthenes with b.p.s between 108 and 142°. For each hydrocarbon a brief description is given of the method of preparation and of the main physical properties (b.p., refractive index, density, and molecular refraction, both found and calculated); all the constants are compared with those of extremely pure preparations of the respective hydrocarbons [7] (given in square brackets), apart from 1,2-dimethyl-4-ethylcyclopentane which was obtained for the first time. The following symbols are used to characterize the Raman lines: br – broad; d – double; r – sharp; ba – line set against a background of considerable intensity; (?) – the possibility is not excluded that the line in question is a repetition of a certain line excited by another one.

Cis, trans, cis-1,2,4-trimethylcyclopentane* was prepared from 2,4-dimethylcyclopenten-2-one which was synthesized by Nazarov's method [8]. The ketone was hydrogenated in presence of skeletal nickel to 2,4-dimethylcyclopentan-1-ol; the latter was oxidized to 2,4-dimethylcyclopentan-1-one which with methylmagnesium iodide was converted to the tertiary alcohol; from the latter by dehydration followed by hydrogenation, of the unsaturated hydrocarbon and fractionation of the hydrogenation products in a column of 60 theoretical plates were isolated cis, trans,cis-1,2,4-trimethylcyclopentane and the below-described cis,cis,trans-1,2,4-trimethylcyclopentane: b.p. 109.2° (760 mm); n_D^{20} 1.4101; d_4^{20} 0.7463; found MR 37.23; calc. for C_8H_{16} MR 36.94 [B.p. 109.08° (760 mm); n_D^{20} 1.41057; d_4^{20} 0.74727.

$\Delta\nu$: 257 (7), 275 (3, br), 331 (0), 405 (5), 422 (5, br), 490 (15, br), 529 (7), 585 (1, br), 769 (44), 811 (8), 824 (8), 836 (2, br), 938 (8), 966 (2), 999 (1), 1027 (3), 1052 (5), 1079 (4), 1093 (2, br), 1148 (13, d), 1225 (0), 1253 (0), 1280 (1), 1308 (6), 1341 (7), 1359 (3), 1459 (48), 2665 (0), 2725 (10), 2848 (90), 2868 (180), 2904 (30, ba), 2925 (130), 2955 (160).

Cis,cis,trans-1,2,4-trimethylcyclopentane was prepared at the same time as the preceding hydrocarbon and separated by fractional distillation. B.p. 116.8° (760 mm); n_D^{20} 1.4185; d_4^{20} 0.7632; found MR 37.06, calculated

* See Diagram A, p. 608.

Diagram A Diagram B Diagram C Diagram D

for C_8H_{16} MR 36.84. [B.p. 116.73° (760 mm); n_D^{20} 1.41854; d_4^{20} 0.76345.] (See Diagram B above.)

$\Delta\nu$: 241 (0), 289 (3, br), 370 (3), 418 (0), 436 (2, br), 498 (14), 520 (9), 748 (17, br), 761 (20), 812 (0), 854 (6), 895 (0), 938 (8), 975 (2), 1023 (3), 1037 (2, br), 1066 (2), 1091 (2), 1148 (5), 1172 (6), 1228 (0), 1313 (8), 1347 (5), 1379 (3), 1459 (44, br), 2729 (5), 2851 (60), 2873 (160), 2904 (100), 2935 (150), 2961 (120).

Cis,cis,trans-1,4-dimethyl-2-ethylcyclopentane.* 2,4-Dimethylcyclopentan-1-one was prepared by the previously described method; from it by the action of ethylmagnesium bromide was obtained the tertiary alcohol which was converted into the unsaturated hydrocarbon as above and then into a mixture of the stereoisomers of 1,4-dimethyl-2-ethylcyclopentane; the latter were fractionated in a column with an efficiency of 60 theoretical plates. Cis,cis,trans-1,4-dimethyl-2-ethylcyclopentane was isolated with b.p. 136.5° (760 mm); n_D^{20} 1.4205; d_4^{20} 0.7637; found MR 41.84; calculated for C_9H_{18} MR 41.56. [The literature does not contain any data for the properties of this hydrocarbon.] (See Diagram C above.)

$\Delta\nu$: 191 (0, br), 264 (2, br, d), 317 (2), 372 (0, br), 402 (1), 420 (5), 445 (3), 483 (5), 524 (3), 560 (0), 746 (2, d), 772 (7), 796 (5), 819 (4, br), 841 (4, br), 927 (0, br), 954 (4), 972 (4), 1043 (6), 1055 (6), 1079 (1), 1095 (2, br), 1149 (9, br), 1198 (0), 1250 (1), 1285 (3), 1311 (3, br), 1348 (6), 1362 (2), 1447 (30), 1462 (55), 2729 (5) 2853 (80), 2870 (160), 2902 (90), 2933 (120), 2958 (120).

Cis,trans,cis-1,4-dimethyl-2-ethylcyclopentane was prepared together with the preceding hydrocarbon and isolated by fractional distillation. B.p. 143.2° (760 mm); n_D^{20} 1.4270; d_4^{20} 0.7795; found MR 41.55; calculated for C_9H_{18} MR 41.56. [There are no data for the properties of this hydrocarbon in the literature.] (See Diagram D above.)

$\Delta\nu$: 200 (0, br), 286 (1), 325 (4), 376 (0, br), 392 (3), 416 (3), 435 (0), 474 (3), 501 (2), 516 (4, br), 536(0), 745 (5), 761 (10), 792 (5), 809 (4), 855 (6), 907 (1), 922 (2), 964 (6, d), 1025 (1), 1042 (8), 1066 (4), 1092 (3), 1150 (5); 1164 (6), 1191 (0), 1228 (1), 1260 (2), 1287 (3), 1313 (4, br), 1361 (4, d), 1445 (20), 1460 (55), 2729 (5), 2854 (70), 2872 (170), 2902 (50), 2935 (180), 2959 (130).

1,1,3-Trimethylcyclopentane was obtained from β-methylcyclopentanone; treatment with methylmagnesium iodide gave the tertiary alcohol which was then converted to the chloride; the latter by reaction with zincdimethyl was transformed into 1,1,3-trimethylcyclopentane. The hydrocarbon was purified by passing through silica gel and was then distilled in a column with an efficiency of 40 theoretical plates. B. p. 105.1° (760 mm); n_D^{20} 1.4110, d_4^{20} 0.7484. found MR 37.20; calculated for C_8H_{16} MR 36.94 [B.p. 104.89° (760 mm); n_D^{20} 1.41115; d_4^{20} 0.74825.]

$\Delta\nu$: 241 (0), 290 (6), 343 (11), 409 (7), 443 (0), 531 (13), 570 (7), 746 (11), 792 (17), 808 (5), 846 (0, br), 936 (11, d), 962 (6), 993 (8), 1041 (1, br), 1059 (4), 1092 (4), 1131 (2), 1176 (7), 1192 (7), 1235 (7, br), 1311 (7), 1351 (1) 1446 (20), 1463 (33), 2718 (10), 2756 (2), 2860 (130), 2893 (80), 2924 (130), 2956 (170).

Trans-1-methyl-3-ethylcyclopentane was prepared from β-methylcyclopentanone; reaction with ethylmagnesium bromide converts it into the tertiary alcohol; the latter is dehydrated and the resultant unsaturated hydrocarbon is hydrogenated and fractionated in a column with an efficiency of 40 theoretical plates. B.p. 120.1° (763 mm); n_D^{20} 1.4185; d_4^{20} 0.7626; found MR 37.09; calculated for C_8H_{16} MR 36.94. [Cis-form, b.p. 120.2° (760 mm); n_D^{20} 1.420; d_4^{20} 0.772. Trans-form: b.p. 120.8° (760 mm); n_D^{20} 1.4186; d_4^{20} 0.7619.]

$\Delta\nu$: 284 (2, br), 303 (4), 394 (14), 425 (5, br), 522 (5), 538 (3), 596 (0), 760 (2, br), 774 (4, br), 837 (18, br), 912 (0), 939 (4), 982 (2), 992 (4), 1007 (2, br), 1040 (5), 1068 (4, br), 1099 (3, br), 1134 (4), 1152 (4), 1176 (0, br), 1248 (1, br), 1284 (3), 1313 (3), 1330 (1), 1355 (3), 1448 (43), 1464 (30), 2729 (5), 2845 (90), 2869 (180), 2903(90), 2927 (130), 2955 (150).

* Contamination with the cis,trans,trans-form is possible. The structure of the cis,cis,trans-form is shown on the diagram by the dense lines; the structure of the cis,trans,trans-form is shown by the broken line.

Cis-1,4-dimethylcyclohexane was prepared by hydrogenation of p-xylene and after passage through silica gel it was separated from the mixture of steroisomers by fractionation in a column with an efficiency of 75 theoretical plates. B. p. 124.5° (760 mm); n_D^{20} 1.4297; d_4^{20} 0.7829; found MR 36.98; calculated for C_8H_{16} MR 36.94. [B.p. 124.321° (760 mm); n_D^{20} 1.42966; d_4^{20} 0.78285.]

$\Delta\nu$: 125 (4), 258 (4), 286 (1), 310 (2), 373 (12, d), 434 (3), 472 (19, d), 637 (18), 760 (95), 788 (17), 897 (0), 925 (3), 954 (15), 976 (8), 1001 (10), 1055 (23), 1095 (10), 1107 (10), 1160 (10), 1170 (10), 1207 (11), 1248 (6), 1263 (23), 1301 (5), 1319 (2), 1344 (13), 1375 (1, br), 1438 (29), 1463 (34), 2668 (0, d), 2724 (3), 2750 (3), 2852 (170), 2873 (50, ba), 2897 (160, ba), 2912 (150, ba), 2929 (290), 2959 (80, br).

Trans-1,3-dimethylcyclohexane* was obtained together with the preceding hydrocarbon and was isolated by fractionation; b.p. 119.5 (760 mm); n_D^{20} 1.4209; d_4^{20} 0.7627; found MR 37.30; calculated for C_8H_{16} MR 36.94 [B. p. 119.351° (760 mm); n_D^{20} 1.42090; d_4^{20} 0.76255.]

$\Delta\nu$: 254 (0), 335 (0), 376 (50), 429 (0), 454 (32), 475 (15), 547 (0), 566 (0), 760 (150), 786 (6), 849 (0), 926 (3), 953 (11), 1005? (4), 1062 (75), 1104 (0), 1166 (20), 1186 (20), 1250 (36), 1264 (2), 1307 (12), 1348 (27), 1361 (15, br), 1436 (13), 1460 (60), 2676 (2, br), 2723 (3), 2748 (1), 2845 (230), 2868 (180), 2911 (120, br), 2926 (230), 2955 (110).

n-Octane** was obtained from 2-octanone, distilled in vacuum in a column with an efficiency of 60 theoretical plates, by dehydration over alumina and hydrogenation over platinized carbon in a duck. The n-octane was fractionated in a column with an efficiency of 60 theoretical plates and has b.p. 125.6-125.7° (760 mm); n_D^{20} 1.3975; d_4^{20} 0.7027; found MR 39.19; calculated for C_8H_{18} MR 39.14. [B. p. 125.667 (760 mm); n_D^{20} 1.39745; d_4^{20} 0.70260.]

$\Delta\nu$: 282 (16), 300 (2, br), 352 (0), 377 (0), 400 (0), 427 (0), 507 (0, br), 707 (0), 730 (0), 766 (1), 813 (2, br), 842 (3), 860 (6), 877 (7), 895 (8), 954 (2, br), 969 (4), 1028 (5), 1044 (5), 1062 (8, r), 1085 (11), 1137 (7), 1165 (2), 1304 (15), 1440 (30), 1459 (30), 2637 (0), 2670 (0), 2732 (5), 2853 (100), 2878 (130, r), 2904 (100, d, ba), 2939 (80), 2964 (45).

2,5-Dimethylhexane*** was prepared by the Wurtz method from isobutyl bromide; it was purified from bromides by shaking with ethanolamine and was distilled in a column with an efficiency of 50 theoretical plates; b.p. 109.4° (760 mm); n_D^{20} 1.3925; d_4^{20} 0.6934; found MR 39.27; calculated for C_8H_{18} MR 39.14. [B. p. 109.106° 760 mm); n_D^{20} 1.39246; d_4^{20} 0.69355.]

$\Delta\nu$: 267 (11, br), 314 (9), 433 (6, br), 451 (8), 683 (0), 725 (0), 764 (0), 777 (10), 798 (2), 825 (5), 839 (31), 881 (1), 907 (5, br), 941 (5), 961 (16), 1037 (3), 1048 (6) 1096 ? (2), 1148 (14), 1172 (14), 1232 (2, br), 1293 (5), 1305 (6), 1338 (17), 1365 (1), 1452 (34, br, d), 1464 (34), 2649 (0), 2719 (5), 2759 (5), 2852 (30), 2872 (180), 2908 (100, ba), 2931 (100, ba), 2961 (140).

EVALUATION OF RESULTS

Special attention is merited by the problem of the structure of the steroisomers of 1,2,4-trimethylcyclopentane, 1,4-dimethyl-2-ethylcyclopentane and 1-methyl-3-ethylcyclopentane which we synthesized. All three possible isomers of 1,2,4-trimethylcyclopentane have been prepared previously [7]. The preparation had the constants:

B.p., °C (760 mm)	n_D^{20}	d_4^{20}
109.28	1.41057	0.74727
116.73	1.4185	0.76345
118	1.422	0.766

In conformity with the Auwers-Skita law, the hydrocarbon with the lowest b.p. was assigned the cis,trans,cis-structure, the next one the cis,cis,trans-structure, and the highest boiling hydrocarbon the cis,cis,cis-structure.

In a recent paper [9] Chiurdoglu and coworkers described the preparation of these three stereoisomers and their Raman spectra, but they deviated from the paper cited above in assigning a different spatial distribution of the side chains to these stereoisomers. Thus, they regard the lowest boiling isomer as the cis,cis,cis-form and the remaining two as trans-forms. It was stated in the paper that proof of this would be published later but the promised

* The previously described [4] spectrum of trans-1,4-dimethylcyclohexane was obtained with a less pure preparation of this hydrocarbon.

** The previously described [1] spectrum of n-octane was obtained with a less pure preparation of this hydrocarbon. The specimen used in the present investigation was synthesized by T. F. Bulanova.

*** The previously described [1] spectrum of 2,5-dimethylhexane was obtained with a very impure preparation of this hydrocarbon.

paper has not yet appeared.

We obtained two stereoisomers of 1,2,4-trimethylcyclopentane to which we attributed the following structures on the basis of the Auwers-Skita law: cis,trans,cis- with b.p. 109.2° (760 mm) and cis,cis,trans- with b.p. 116.8° (760 mm). Comparison of the constants and Raman spectra of our preparation of cis,cis,trans-1,2,4-trimethylcyclopentane with the spectra of Chiurdoglu's preparation shows that our preparation does not contain any appreciable amount of the higher boiling isomer (cis,cis,cis-form). Actually the spectrum of our preparation is lacking in the frequency of 865 cm^{-1}, with intensity 2 in the visual scale, which is characteristic (according to the data of the Belgian investigators) of the higher boiling isomer. Some other frequencies characteristic of the latter isomer, but less intense are also absent from the spectrum of our preparation.

It should be noted that the spectrum of our preparation contains the intensive frequency 761 cm^{-1} which, according to Chiurdoglu's data, is present in the cis,cis,cis-form but absent from the cis,cis,trans-form. We may assume, however, that this frequency occurs in the spectra of all three stereoisomers and was not detected by the Belgian investigators in the case of the cis,cis,trans-form due to the low resolving power of their spectrograph. Indeed for the latter isomer they observed a broad band at 751 cm^{-1} whereas we detected two closely located frequencies at 748 and 761 cm^{-1} of which the first was broad.

The data at our disposal for the Raman spectra of the stereoisomers of 1,2,4-trimethylcyclopentane enable us to draw conclusions about the spatial arrangement of the side chains in the two stereoisomers of 1,4-dimethyl-2-ethylcyclopentane which we separated and which may even exist in four forms. The repeated presence of characteristic frequencies in molecules of similar structure but with different chain lengths is a well-established fact [3, 4, 5, 6, 10]. It is known that in homologs of cyclopentane and benzene with one side chain as well as with two side chains, a series of closely repeating frequencies is observed. In Tables 1 and 2 are set forth as an example the principal frequencies (in cm^{-1}) and intensities of molecules of analogous structure but with different side chains. This observation has great practical significance; it sometimes permits the utilization of characteristic frequencies in the solution of specific problems of analysis and structure.

TABLE 1

m-Xylene	1-Methyl-3-ethylbenzene
539 (230)	530 (85)
726 (440)	721 (210)
1000 (540)	1002 (420)

TABLE 2

p-Xylene	1-Methyl-4-ethylbenzene
459 (200)	462 (20)
810 (110)	807 (140)
829 (410)	826 (140)
1205 (330)	1202 (160)

As we know, however, the concept of characteristic frequencies must not be unduly simplified and the occurrence of similar or repetitive frequencies must by no means be always regarded as a trustworthy criterion of group structure. A specific confirmatory indication of an empirical character in this connection is the reproducibility not only of the frequency but also of other characteristics of the investigated lines (intensity, polarization and width). The most trustworthy criterion of the suitability of empirical group indications is the development of theoretical methods of calculation of the vibrations of complex molecules which, aided by parameters determined from the spectra of a series of compounds, enable more or less detailed conclusions to be drawn about the spectra of more complex compounds. Such methods of calculation have been developed in the case of paraffins but are unfortunately lacking for other types of compounds, and we were compelled to make cautious use of purely empirical features. The reliability of the latter certainly increases with the accumulation of experimental material. In some cases, however, even relatively limited data may be turned to good account.

In this investigation the above-mentioned spectroscopic criterion was used for elucidation of the structure of the stereoisomers of 1,4-dimethyl-2-ethylcyclopentane and 1-methyl-3-ethylcyclopentane which we prepared, a problem that would have been extraordinarily difficult to solve by purely chemical methods. The structures were established by comparing the Raman spectra of our hydrocarbons with the spectra of hydrocarbons of similar structure, the spatial arrangement of whose side chains had been previously determined from chemical data. In Table 3 are given the frequencies and intensities of the principal lines of the trialkylcyclopentanes which were studied.

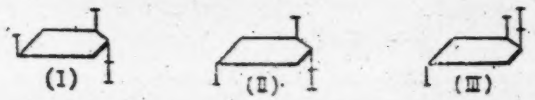
A comparison of the frequencies set forth in Table 3 clearly shows the resemblance between the spectrum of cis,trans,cis-1,2,4-trimethylcyclopentane and that of the lower boiling isomer of 1,4-dimethyl-2-ethylcyclopentane. The spectrum of cis,cis,trans-1,2,4-trimethylcyclopentane is likewise very similar to that of the higher

TABLE 3

Cis,trans,cis-1,2,4-trimethylcyclopentane	1,4-Dimethyl-2-ethyl-cyclopentane, isomer with b.p. 136.5°	Cis,cis,trans-1,2,4-trimethylcyclopentane	1,4-Dimethyl-2-ethyl-cyclopentane, isomer with b.p. 143.2°
422 (5)	420 (5)	498 (14)	501 (2)
490 (15)	483 (5)	520 (9)	516 (4)
529 (7)	524 (3)	748 (17)	745 (5)
	746 (2)	761 (20)	761 (10)
769 (44)	772 (7)	854 (6)	855 (6)
811 (8)	819 (4)		

boiling isomer of 1,4-dimethyl-2-ethylcyclopentane. In both cases the replacement of the methyl group by ethyl does not lead to a substantial change of frequencies; changes are only observed in the intensities, which in these cases diminish appreciably.

Consequently the lower boiling isomer evidently possesses the structure of cis,cis,trans-1,4-dimethyl-2-ethylcyclopentane (I). The spectrum of this hydrocarbon, however, contains the frequency of 746 cm^{-1} which has no analog in the spectrum of cis,cis,trans-1,2,4-trimethylcyclopentane. It is very probable that this frequency belongs to the spectrum of cis,trans,trans-1,4-dimethyl-2-ethylcyclopentane (II) which is bound to have a boiling point very close to that of the cis,cis,trans-form and which we were probably unable to separate from the latter.



By the same reasoning the higher boiling isomer must be cis,trans,cis-1,4-dimethyl-2-ethylcyclopentane (III). It should be noted that the spectrum of our preparation does not contain any frequency similar to the frequency of 865 cm^{-1} which, as mentioned above, is characteristic of cis,cis,cis-1,2,4-trimethylcyclopentane. We may therefore conclude that in the case of 1,4-dimethyl-2-ethylcyclopentane as well as of 1,2,4-trimethylcyclopentane, the cis,cis,cis-form is not present in our preparation.

A comparison carried out in a similar manner of the spectrum of our preparation of 1-methyl-3-ethylcyclopentane with the spectral data in the literature for the cis- and trans-forms of 1,3-dimethylcyclopentane, also a comparison with our data for the mixture of stereoisomers of this hydrocarbon and for the mixture of cis-trans-forms of 1-methyl-3-n-propylcyclopentane previously obtained by us, enable the trans-form to be assigned to our preparation. The hydrocarbons 1,3-dimethylcyclopentane and 1-methyl-3-n-propylcyclopentane, respectively the cis- and trans-forms, have the following characteristic frequencies: first hydrocarbon – 803 and 828 cm^{-1}; second – 817 and 832 cm^{-1}. The 1-methyl-3-ethylcyclopentane that we investigated has the frequency 837 cm^{-1} which is close to the frequency characterizing the trans-form.

In conclusion we take this opportunity of conveying our sincere gratitude to G. S. Landsberg for valuable advice in the course of the work.

SUMMARY

1. Details of the Raman spectra are given of seven cyclopentane and cyclohexane hydrocarbons, including two hydrocarbons synthesized for the first time. All the intensities of the Raman frequencies are set forth in a uniform scale.

2. The spectroscopic data served as a basis for evaluation of the problem of the spatial arrangement of the side chains in 1-methyl-3-ethylcyclopentane and in the stereoisomers, synthesized for the first time, of 1,4-dimethyl-2-ethylcyclopentane.

3. New data are presented for the Raman spectra of three hydrocarbons for which data had previously been obtained on the basis of less pure specimens.

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HIGH MOLECULAR COMPOUNDS OF PETROLEUM

COMMUNICATION 1. APPLICATION OF COLOR PHOTOGRAPHY TO THE CHARACTERIZATION OF LUMINESCENCE

S. R. Sergienko, Yu. A. Bedov and M. P. Teterina

Chemical and physical advances have made possible the investigation of complex organic compounds containing hundreds and thousands of atoms in their molecules. The chemistry of high-molecular compounds, stemming from organic chemistry, has enabled closer investigation of the chemical properties and structure of numerous natural substances.

The chemistry of high-molecular compounds has developed a number of new methods of resolution and examination of the giant molecules of complex organic compounds. In these studies a particularly important part has been played by physical methods. The usual effect of reactive chemicals and high temperatures upon high-molecular compounds is to change their composition, structure and molecular weight. This is particularly true of high-molecular compounds containing nitrogen, sulfur and oxygen which are consequently distinguished by exceptional instability under the influence of high temperatures and of chemically active agents. It is particularly important when studying such unstable high-molecular organic compounds to employ the mildest methods in order to exclude chemical transformations during the very process of investigation. With this objective, many purely physical methods of resolution and investigation of high-molecular substances have been proposed.

Up to recently petroleum had not been subjected to examination by the special methods developed by the chemistry of high-molecular compounds. This is because industrial use has been made of the low-molecular and middle fractions of petroleum, whereas the heavier portion of petroleum, in which are concentrated the high-molecular hydrocarbon and asphaltene-resin constituents, have remained waste products of the industry. In the early stages of its development, the petroleum processing industry repeated the historical course of organic chemistry: in both cases, that which could not be distilled without decomposition was called " resin" and was rejected as undeserving of the attention of the chemist. These high-molecular "resinous" organic compounds have actually now become the objects of investigation of the chemistry of high-molecular compounds.

Today one of the most important scientific and technological problems of petroleum processing is that of the complete, i.e. residueless, processing and utilization of petroleum as a chemical raw material. Consequently the high-molecular, resinous portion of petroleum, amounting to 10-50% of the total, depending on the source, must be included in the processing scheme. In order to use this complex chemical raw material in industry to the best advantage, a detailed study is necessary of its chemical composition, structure and principal reactions. That is why the chemistry of high-molecular compounds of petroleum has now acquired such wide importance.

Unlike such high-molecular compounds as rubber, cellulose, etc., the high-molecular compounds of petroleum are characterized by relatively low molecular weights (500-5000) and by the absence of a fundamental structural unit whose polymerization could lead to a chain-like giant molecule containing regularly repeated structural links. In spite of their relatively low molecular weight, the high-molecular compounds of petroleum are distinguished by extremely low stability to chemical and thermal action. This behavior must be taken into consideration when separating the complex mixture of high-molecular compounds of petroleum.

The method of adsorption chromatography of Tsvet [1] was proposed a long time ago for the separation of the resin-asphaltenic substances of petroleum from the hydrocarbons for the purpose of their quantitative determination. Utilization of silica gel as an adsorbent for the resins has acquired great popularity, ever since the work of Gurvich [2] and Sakhanov and Vasilyev [3], both for analytical and processing purposes in the petroleum industry. Total separation of the resins of petroleum products with the help of an adsorbent such as silica gel has been effected with full success.

The study of the composition and chemical nature of the main components of the high-molecular substances of petroleum necessitates in the first place their resolution into narrower fractions. For this purpose advantage is

taken of the differing solubility and adsorbability of the constituents of the resin-asphaltene portion of petroleum. Chernozhukov and Luzhetsky [4] used phenol as the selective solvent for separation of the resins. Tilyupo and Chernozhukov [5] effected resolution of petroleum resins by adsorptive chromatography on silica gel followed by fractional desorption of the resins from the silica gel with organic solvents and by further resolution of the obtained fractions into phenol-soluble and phenol-insoluble substances.

EXPERIMENTAL

In our studies of high-molecular compounds of petroleum we likewise made use of a combined scheme of separation of hydrocarbons and resins based on the differing absorbability on silica gel of the individual components of this complex mixture of organic compounds and also on their differing extractability by organic solvents. The general scheme of separation, as modified by us (Fig. 1), permitted first of all a sufficiently complete separation from the mixture of the hydrocarbon portion, and then a closer fractionation of the resin adsorbed onto silica gel with the help of extracting liquids of differing polarities and of a selectively acting solvent (phenol). The application of adsorption analysis to the hydrocarbon portion permitted the characterization of its group composition [6].

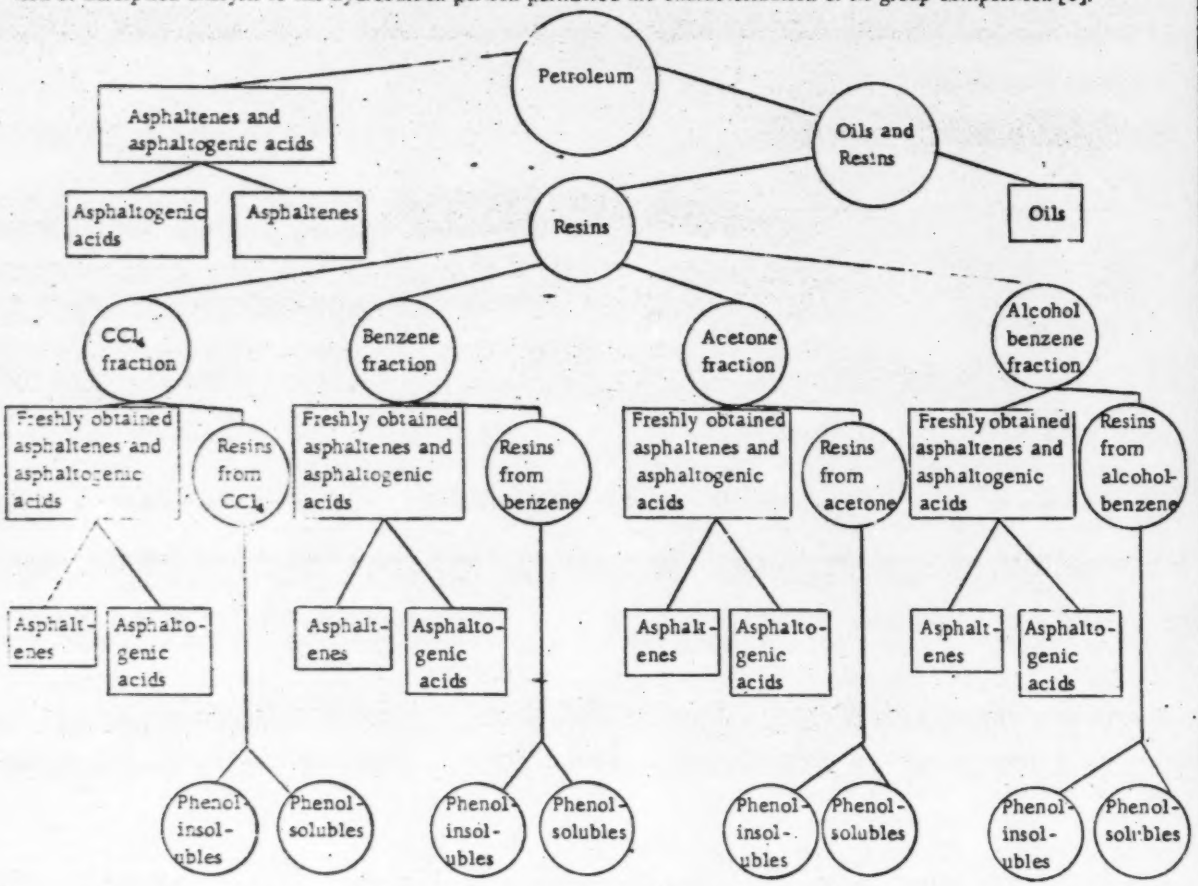

Fig. 1. General scheme for resolution of the resin-asphaltenic portion of petroleum.

We have already described in detail [7] the procedure for resolution of the high-molecular portion of petroleum. It involves subjecting the petroleum or petroleum product to investigation after preliminary freeing from asphaltenes by 40-fold dilution with isopentane and filtering through a silica gel column (fraction of silica gel retained on 32 meshes-to-the-inch screens). After washing the hydrocarbon portion with ligroine, the resins adsorbed on the silica gel were fractionally extracted from the silica gel by successive treatment with a series of organic solvents of gradually increasing polarity (carbon tetrachloride, benzene, acetone, 1:1 alcohol/benzene mixture). The obtained resin fractions were later freed from solvents and subjected to treatment with phenol for separation into phenol-soluble and pheol-insoluble portions. The resin fractions obtained by this procedure were characterized by determinations of molecular weight, acidity, content of unsaturateds, chemical composition and type of luminescence.

Luminescence Analysis

Although the luminescence method of characterization of substances also suffers from the drawback that the luminescence is insufficiently specific and cannot be such a decisive characteristic of substances as the adsorption spectra or Raman spectra, it nevertheless proves to be suitable and useful for observation of the qualitative changes taking place in a substance, particularly in the case of petroleum resins, due to various chemical and physical interactions (oxidation, hydrogenation, resolution into fractions, etc.). With consumption of very little material, luminescence analysis permits the observation of qualitative changes in a substance with the help of the change in the character of the luminescent radiation.

For the observation of luminescence we made use of the method of paper chromatography. Strips of filter paper were first extracted in a Soxhlet apparatus with alcohol-benzene mixture for 6 hours to eliminate luminescing impurities. The so-prepared filter paper strips of width 1 cm and length 15-20 cm were suspended over small beakers into each of which was poured 5 ml of 0.001% solution of the resin sample in 1:1 alcohol-benzene. The filter paper strips were suspended in such a manner that they did not touch the walls of the beaker and were immersed in the solution to the bottom. The samples were left in this state for 12-14 hours (usually overnight). During this period the surplus solvent evaporated from the beaker and also the solvent imbibed by the paper. The dry samples were inspected in the light of a PRK-2 quartz lamp filtered through a FS-4 light filter transmitting only blue and ultraviolet rays.

Our observations of the luminescence revealed a number of characteristics of the samples of resins which had been subjected to various treatments. However, up to now attempts to objectively represent the observed picture of the luminescence or to describe it have proved unsuccessful. Drawings of the luminescence picture, apart from the enormous labor and the special abilities that they demand from the artist, suffer from subjective transfer, since they depend on the color perception of the investigator. Each time that it is necessary for a communication about an observed luminescence picture to be sent to a printer or elsewhere, it is necessary either to prepare the appropriate specimens and start up the luminescence lamp or to limit oneself to a description, in which event the picture loses all its objectivity and significance. We therefore undertook experiments to obtain a permanent record of the luminescence of the paper chromatogram of the resin solutions by color photography.

Photographs were taken with a "Kiev" camera on DS-1 color negative film supplied by a Russian manufacturer. The set-up for the photography is shown in Fig. 2.

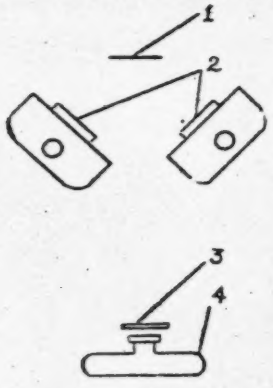

Fig. 2. Set-up for luminescence photography: 1) screen with samples; 2) PRK-2 lamp with FS-4 filter; 3) lead glass; 4) "Kiev" camera

All the color materials were processed by the usual methods used in color photography. The specimens were irradiated from two sides with PRK-2 quartz lamps through FS-4 light filters. For absorption of the ultraviolet rays, reflected from the lens of the camera and causing appearance of a blue tone on the photograph, in front of the lens of the camera was placed an ultraviolet absorption filter. For this purpose we tried out a series of color filters. We used a color filter film, made by the Agfa firm, and liquid color filters. In addition, as color filters we used lead glass 12 mm thick. The liquid color filter was constructed in the following manner: a cell 25 mm thick with parallel walls of ordinary glass, open at the top, was filled with one of the substances. Care was taken during filling to ensure that air bubbles did not adhere to the sides and did not distort the photograph. As the filling liquids we used distilled water, saturated solution of common salt and carbon bisulfide which had a fairly high absorption in the blue and near ultraviolet region of the spectrum. By the same token (absorption in the blue and near ultraviolet region of the spectrum), Agfa light filters [8] were selected whose absorption curves are shown in Fig. 3.

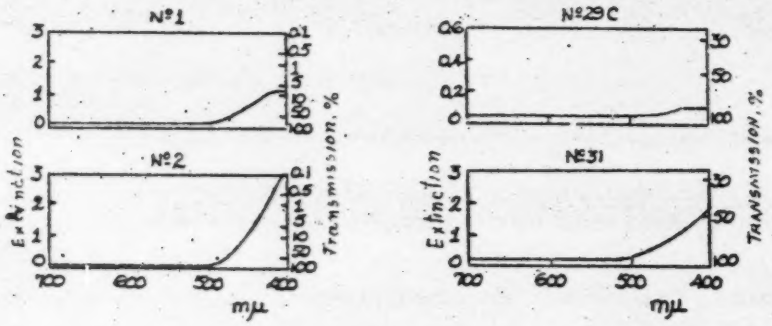

Fig. 3. Absorption curves of Agfa light filters.

In Figures 4 and 5 are shown photographs of the luminescence of specimens of resins taken with various light filters. Prints were made without the use of correcting filters during printing. Examination of the photographs shows that the Agfa No. 31 filter does not completely remove the blue background and considerably reduces the intensity of the yellow luminescence band. Agfa No. 1 filter and the liquid filters containing sodium chloride solution and distilled water gave a similar result and therefore the corresponding prints are not reproduced. Agfa No. 29 filter gives relatively good light transmission of the colored zones but also lowers the intensity of the yellow luminescence. The most successful results were got when using Agfa No. 2 filter, the liquid carbon disulfide color filter and lead glass. Since of these the most readily available and the simplest in use was lead glass, and since the quality of the pictures obtained with the other filters was not superior, we decided to use lead glass in all the later work. Photographs of the luminescence of various specimens of resins are reproduced in Figs. 6 and 7. Inspection of these photographs shows that the method of observation of color photographs of luminescence enables differentiation between specimens of resins containing asphaltenes and those not containing asphaltenes. In the working-up of resin fractions with phenol, leading to enrichment of the phenol-soluble portion with aromatic, sulfur and oxygenated compounds, the yellow band of luminescence for the phenol-soluble resins contracts and becomes covered with a non-luminescing layer. Conversely, for the pheno-insoluble resins, the yellow luminescent band broadens and becomes more intense. In the specimens of oxygenated resins, on the color photographs of the luminescence, darkening is observed of nearly the whole of the luminescent region; the light-yellow tones are replaced by a conspicuously orange color, in the case of hydrogenated resins however, the color becomes more light-yellow and the blue band of luminescence characteristic of polycyclic hydrocarbons is developed.

Of very great interest are the color photographs of the luminescent picture of high-molecular hydrocarbons "light" oils and "dark" oils isolated with the help of adsorption chromatography and characterized by us previously. The so-called light oil contains predominantly naphthenic-paraffinic hydrocarbons and gives a light-blue luminescence. The "dark" oils, however, consisting almost completely of aromatic hydrocarbons (mono- and bicyclic) with a small admixture of resins, give a yellow luminescence similar in character to the luminescence of the resins.

To minimize the risk of image distortion during the positive process, we made attempts to take photographs on reversal film. Due, however, to the difficult availability of the film and the possibility of obtaining only one picture which could not be duplicated, we had to abandon this method although it gave good results. Attempts to reverse negative film and photographic paper have not yet given satisfactory results.

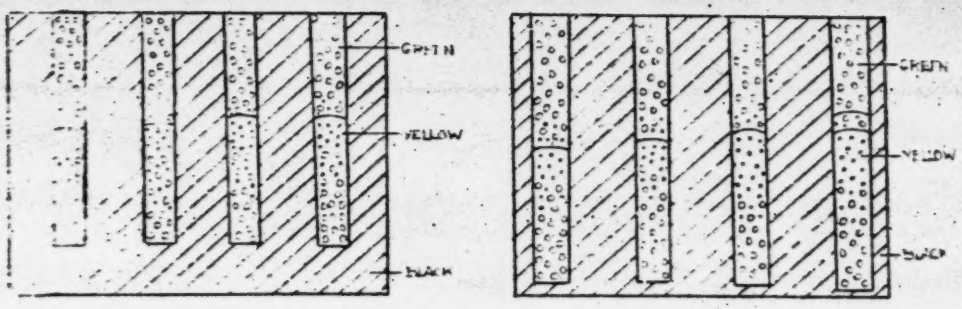

Fig. 4. Photographs* of luminescence of specimens of resins, taken with various Agfa filters:
1 – Agfa No. 31. 2 – Agfa No. 29.

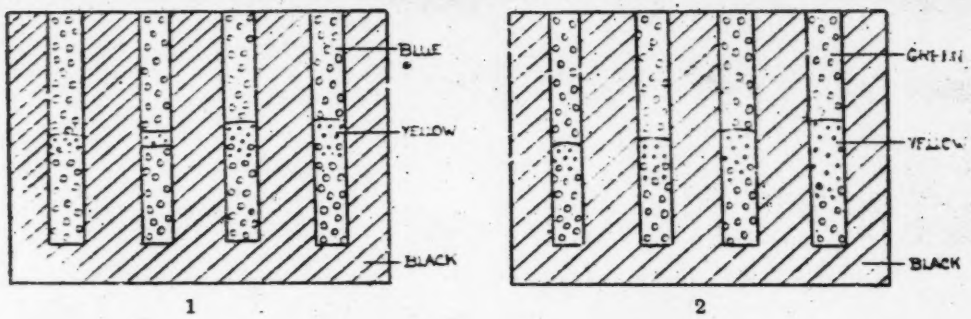

Fig. 5. Photographs* of luminescence of samples taken with various filters:
1 – CS2 filter. 2 – Lead glass filter.

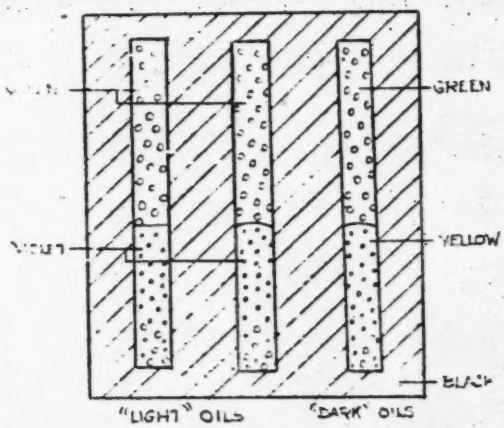

Fig. 7. Photographs* of luminescence of various samples of high-molecular hydrocarbons of Romashk petroleum.

* The color photographs accompanying this paper in the original could not be reproduced in color by the process used to publish this translation. Reproduction in black-and-white would have completely distorted the relative size of areas in the spectra. We have therefore interpreted these photographs in this manner, so that the relative areas of luminescence referred to in the text might be apparent. Publisher.

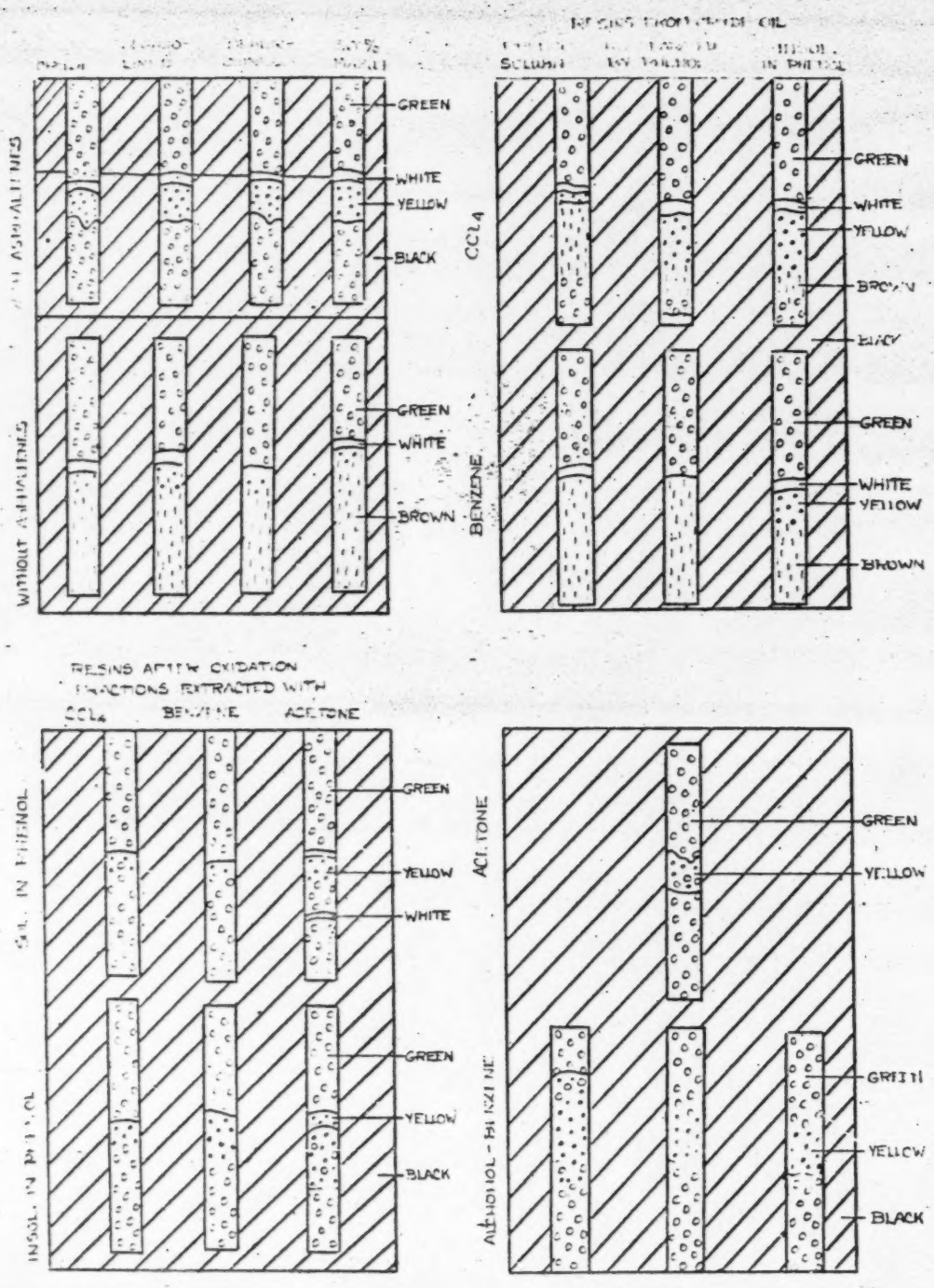

Fig. 6. Photographs of luminescent radiation of various samples of Smolromashk oil.

From the results set forth above we see that the application of color photography to the permanent recording of luminescence pictures opens up the possibility of eliminating the influence of the subjective judgement of the observer on the luminescence. It has to be admitted that up to now we have not succeeded infully reproducing the original luminescent colors. The photographs do, however, enable the representation of the relative intensity of the radiation, the zonal widths and some other features. We therefore hope that the method here published will prove useful for all workers in the field of luminescence chromatography.

SUMMARY

1. Permanent recording of the luminescence picture with the help of color photography provides the possibility of fully objective assessment of the qualitative difference in the luminescent radiation of various components of the high-molecular resinous compounds of petroleum.

2. Lead glass is a satisfactory and convenient filter which retains the ultraviolet rays and thereby eliminates their influence on the photographic film.

3. The supplementing by color photography of luminescence analysis is an objective method for qualitative evaluation of the chemical changes in the components of the high-molecular resins of petroleums.

Institute of Petroleum of the Academy of Sciences of the USSR Received September 20,1953

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SYNTHESIS AND PHYSICAL AND CHEMICAL PROPERTIES OF VINYLETHYNYLSILANES

A. D. Petrov, S. I. Sadykhzade and Yu. P. Egorov

The dimer of acetylene – 1-buten-3-yne – is used as a raw material for the production of the synthetic rubber known as chloroprene; it also condenses with ketones to form readily polymerizable carbinols applicable as glues.

The organomagnesium compound of 1-buten-3-yne (readily condensable with aldehydes and ketones) is not capable, however, of undergoing the Grignard-Würtz condensation either with primary, secondary or even tertiary alkyl halides. Exceptions, as shown by Carothers and Nieuwland, are such active halides as triphenylchloromethane [1] and allyl bromide [2]. The synthesis of saturated and aromatic tetrasubstituted silanes is effected, as we know, on the basis of $SiCl_4$ and its mono-, di- and trisubstituted derivatives whose halogen-atoms are substituted with facility by both aliphatic and aromatic radicals. We investigated the condensation of 1-buten-3-ynyl magnesium halide with such active halides as alkyl- and arylhalosilanes. It was established that this reagent indeed interacts with high yields with R_3SiCl, R_2SiCl_2 and $RSiCl_3$ and even with $SiCl_4$ but does not condense with primary or even with α- and β-secondary silicon halides of the type of:

$$\gtrless Si-CH_2-X, \quad \gtrless Si-\underset{\displaystyle CH_3}{\underset{|}{CH}}-X, \quad \gtrless Si-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-X$$

The so-prepared vinylethynylsilanes were readily polymerized. We thus found a route to silicohydrocarbons of the enyne type with similar properties to the oxygen-containing derivatives of 1-buten-3-yne or the so-called carbinols.

The first reference to vinylethynylsilanes, specifically to 1-triethylsilyl-3-methyl-3-penten-1-yne, was made by the English physicist Bowden [3]. Petrov and Sadykhzade reported [4] the synthesis by condensation of $MgBr-C\equiv C-CH=CH_2$ with R_3SiCl of four trialkylvinylethynylsilanes, while by condensation with R_2SiCl_2 they obtained three dialkyldivinylethynylsilanes. The physical properties of these seven compounds are set forth in Table 1.

In connection with the chemical properties of these silanes, Kucherov observed the inability to be hydrogenated of the triple bond in the α-position to the silicon (in more drastic conditions there is rapid decomposition of the ketone with the carbonyl group in the β-position as formed); later he noted the addition of both two and four atoms of bromine followed by cleavage of HBr in the latter case. These data as well as the study of the synthesis and properties of silicoacetylenic hydrocarbons of Frisch and Joung [5] permit us to conclude that in the case of vinylethynylsilanes the bromine only adds on at the triple bond. It was also established that vinylethynylsilanes are easily hydrogenated over palladium oxide both fully to butylsilanes and selectively with absorption of two or four atoms of hydrogen. In the former case the main product of hydrogenation was trialkylbutadienylsilane, as was confirmed by the formation with maleic anhydride of an adduct with m.p. 132°. When four hydrogen atoms were absorbed the main product was trialkyl-2-butenesilane as was confirmed by the examination of its Raman spectrum (see below).

We also obtained a series of aliphatic-aromatic vinylethynylsilanes; their physical properties are set forth in Table 2. Concerning their chemical properties, interest is attached to their polymerization tendency which is lower than that of trialkylvinylethynylsilanes and especially great in the case of dimethyl-p-tolyl-vinylethynylsilane. It is also interesting to note that triphenylchlorosilane, in the usual conditions at any rate, (as used by us for condensations of all three substituted halosilanes with $MgBrC\equiv C-CH=CH_2$ at relatively low temperatures below 100°), failed to condense. This fact illustrates the known contrast in properties between $(C_6H_5)_3 \cdot CCl$ (I) and $(C_6H_5)_3 \cdot SiCl$ (II), and between $(CH_3)_3CCl$ (III) and $(CH_3)_3 \cdot SiCl$ (IV). The first halide condenses with $MgBrC\equiv C-CH=CH_2$, the second does not condense [and the sole product of reaction is $(C_6H_5)_3SiOH$ with m.p. 151°], the third does not condense, and the fourth condenses with high yield. These facts illustrate the wide diversity of properties of the tertiary halides and of the corresponding silicohalides formed from them by the Grignard-Würtz reaction.

TABLE 1

Properties of Trialkylmonovinylethynylsilanes and Dialkyldivinylethynylsilanes

Substance	B.p. in °C (in mm mercury)	d_4^{20}	n_D^{20}	MR found	MR calculated*	Yield %	Found (%) C	Found (%) H	Found (%) Si	Calculated (%) C	Calculated (%) H	Calculated (%) Si
Trialkylmonovinylethynylsilanes												
Trimethylvinylethynylsilane $(CH_3)_3Si-C\equiv C-CH=CH_2$	52-53 (80)	0.7714	1.4510	43.35	42.09 43.39	55.0	67.04	10.12	–	67.60	9.81	–
Triethylvinylethynylsilane $(C_2H_5)_3Si-C\equiv C-CH=CH_2$	74-76 (20)	0.8145	1.4695	56.93	55.98 57.28	52.7	72.41	11.40	15.91	72.22	10.90	16.84
Tripropylvinylethynylsilane $(C_3H_7)_3Si-C\equiv C-CH=CH_2$	87-89 (7)	0.8173	1.4700	71.13	69.87 71.17	51.6	74.81	11.70	12.85	74.92	11.61	13.46
Tributylvinylethynylsilane $(C_4H_9)_3Si-C\equiv C-CH=CH_2$	108-110 (8)	0.8201	1.4700	85.18	83.76 85.06	53.1	–	–	11.82	–	–	11.26
Dialkyldivinylethynylsilanes												
Dimethyldivinylethynylsilane $(CH_3)_2Si-(C\equiv C-CH=CH_2)_2$	67-68 (9)	0.8495	1.5108	56.49	53.90 56.50	57.2	74.58	8.08	17.	74.96	7.96	17.50
Diethyldivinylethynylsilane $(C_2H_5)_2Si-(C\equiv C-CH=CH_2)_2$	84-86 (8)	0.8556	1.5140	66.22	63.16 65.76	38.4	76.96	8.7	–	76.47	8.52	–
Dipropyldivinylethynylsilane $(C_3H_7)_2Si-(C\equiv C-CH=CH_2)_2$	84-85 (5)	0.8561	1.5145	76.12	72.42 75.02	36.4	77.70	9.11	13.28	77.67	9.24	12.94

* The first of the pair of values was calculated on the basis of [11] the refraction of the Si–C bond was assumed to be equal to 2.5 just as for the alkylsilanes. The lower value corresponds to the mean value of the Si–C bond, assumed to be equal to 3.8 when C is attached to the $-C\equiv C-\underset{H}{\overset{}{C}}=\underset{H_2}{\overset{}{C}}$ radical.

TABLE 2 Properties of Dimethylarylvinylethynylsilanes

Substance	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}	Yield (%)	Found % C	Found % H	Found % Si	Calculated % C	Calculated % H	Calculated % Si	MR Found	MR Calculated
Dimethylphenylvinylethynylsilane $(CH_3)_2C_6H_5Si-C\equiv C-CH=CH_2$	83-84 (6.5)	0.9229	1.5391	69.2	77.50	7.38	14.80	77.35	7.52	15.08	63.25	63.06
Dimethylbenzylvinylethynylsilane $(CH_3)_2(CH_2C_6H_5)Si-C\equiv C-CH=CH_2$	111-112 (11)	0.9185	1.5391	60.6	78.15	7.95	13.33	77.91	7.99	14.00	68.33	68.69
Dimethyltolylvinylethynylsilane $(CH_3)_2(CH_3C_6H_4)Si-C\equiv C-CH=CH_2$	112-113.5 (10)	0.9147	1.5368	69.6	77.89	7.93	14.20	77.91	7.99	14.00	68.37	68.69
Dimethyl-α-naphthylvinylethynylsilane $(CH_3)_2\alpha\text{-}C_{10}H_7Si-C\equiv C-CH=CH_2$	146-147.5 (6)	1.0116	1.6029	45.4	80.84	6.97	10.87	81.27	6.87	11.77	80.25	79.56

MR is calculated on the basis of new data for the Si−C bond when in the case of $\equiv C-\underset{H}{\overset{|}{C}}=\underset{H_2}{\overset{|}{C}}$ it is equal to 3.8

TABLE 3 Properties of Halogeno- and Alkoxy Derivatives of Vinylethynylsilanes

Substance	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}	MR Found	MR Calc.	Yield (%)	Found % C	Found % H	Found % S	Found % Cl	Calculated % C	Calculated % H	Calculated % S	Calculated % Cl
Methylvinylethynyldichlorosilane $CH_3(CH_2=CH-C\equiv C)SiCl_2$	49-50 (24)	1.0871	1.4760	42.83	42.65	29.7	–	–	–	43.10	–	–	–	43.03
Methyldivinylethynylmonochlorosilane $CH_3(CH_2=CH-C\equiv C)_2SiCl$	88-89 (12)	0.9471	1.5224				–	–	–	16.92	–	–	–	19.65
Vinylethynyltrichlorosilane* $CH_2=CH-C\equiv C\cdot SiCl_3$	67-69 (60)					22.3	–	–	–	56.96	–	–	–	57.42
Vinylethynyltriethoxysilane $(CH_2=CH-C\equiv C)Si(OC_2H_5)_3$	78-79 (7)	0.9407	1.4352	59.47	59.56	34.0	56.84	8.15	11.56	–	56.14	8.45	13.0	–

* This compound fumes in the air and is instantaneously hydrolyzed by atmospheric moisture, due to which circumstance its physical properties could not be determined. The MR was calculated on the basis of new data for the magnitudes of the Si−C bond = 3.8, in the case of the $\equiv Si-C\equiv C-\underset{H}{\overset{|}{C}}=\underset{H_2}{\overset{|}{C}}$ radical.

Attempts to carry out the condensation of $MgBrC{\equiv}C-CH{=}CH_2$ with the primary silicohalide, siliconeopentyl chloride $(CH_3)_3Si \cdot CH_2 \cdot Cl$, proved unsuccessful and we were unable to introduce a triple bond in the β-position to the silicon. But the condensation of the Grignard reagent from this silicohalide with dimethylvinylethynylchloromethane was successful and gave an enynic silicohydrocarbon with a triple bond in the γ-position to the silicon-dimethylsiliconeopentyl-vinylethynylmethane,

$$(CH_3)_3Si{\cdot}CH_2MgCl + Cl-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-C{\equiv}C-CH{=}CH_2 \rightarrow (CH_3)_3SiCH_2 \cdot \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-C{\equiv}C-CH{=}CH_2$$

The Raman spectrum was plotted of the silicohydrocarbon [b.p. 67–69° (6 mm); d_4^{20} 0.8088, n_D^{20} 1.4725. Found %: C 73.40, H 11.01; Si 14.7. Calculated %: C 73.37; H 11.18; Si 15.4]. The following intense frequencies were found: 696 (3), 1290 (5), 1610 (5), 2217 (6), 1407 (3), 1466 (6). Attention should be drawn to the considerable increase of the frequency of C≡C to 2217 cm^{-1}, by comparison with the value of 2158 cm^{-1} when the vinylethynyl group is linked directly with Si. The low yield of the silicohydrocarbon prevented its more detailed study.

Bearing in mind that according to the data of Pudovik and Mukhamedova [6] an analogous reaction in the hydrocarbon series:

$$C_2H_5MgBR + Cl-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-C{\equiv}C-CH{=}CH_2 \rightarrow CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-C{=}C-CH{=}CH_2$$

took place with partial isomerization of the acetylene linkage

$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-C{=}C-CH{=}CH_2 \rightleftarrows CH_3-\underset{\underset{CH_3}{|}}{C}{=}\underset{\underset{CH_3}{|}}{C}-CH_2-CH{=}CH_2$$

it is highly probable that in our case a partial isomerization of this type took place.

Since it appeared to us that the vinylethynyl radical, like the vinyl and allyl radicals, is of interest not only in purely hydrocarbon chains of polymers but also in siloxane chains, we synthesized methylvinylethynyldichlorosilane, methyldivinylethynylmonochlorosilane, vinylethynyltrichlorosilane and triethoxyvinylethynylsilane. The physical properties of these compounds are set forth in Table 3.

Data for the Raman spectra and infrared absorption spectra of the vinylethynylsilanes which we synthesized are set forth below and plotted in the diagrams.

1. Trimethylvinylethynylsilane cm^{-1}: 301 (5 ba), 570 (25), 611 (25), 674 (10), 728 (14 br), 972 (12 br), 922 (10), 1014 (12 br), 1110 (15), 1232 (25 br), 1290 (25), 1353 (3), 1392 (1), 1410 (45), 1460 (24), 1595 (38), 1611 (70), 2154 (210), 2217 (15), 2880 (90), 2908 (45), 2939 (40), 2961 (45), 3015 (42), 3105 (23).

2. Methylethylvinylethynylsilane cm^{-1}: 300 (5 ba), 579 (30), 630 (30), 649 (22), 682 (8), 710 (8), 748 (18 br), 835 (9), 885 (2), 927 (10), 972 (7), 1014 (5), 1110 (20), 1233 (12), 1257 (8), 1290 (26), 1353 (6), 1410 (50), 1460 (8), 1598 (58), 1611 (58), 2145 (48), 2154 (250), 2217 (15), 2880 (25), 2908 (40 br), 2940 (10), 2965 (35), 3015 (45), 3104 (25).

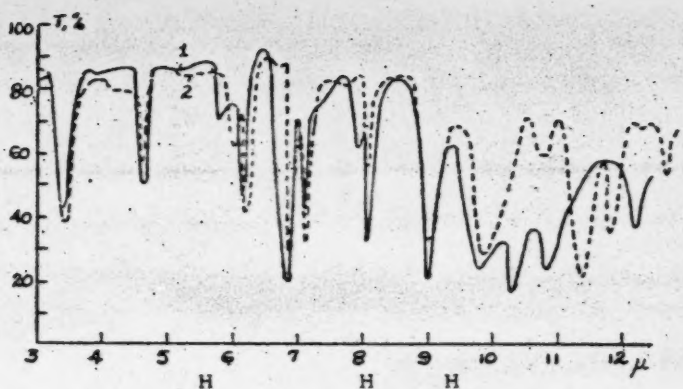
3. Methyldivinylethynylsilane cm^{-1}: 300 (8), 580 (25), 602 (6), 685 (20 br), 742 (25), 761 (2), 835 (10), 884 (10), 925 (8), 961 (8), 1054 (2), 1110 (27), 1253 (10), 1290 (31), 1352 (5), 1410 (70), 1595 (85), 1611 (33), 2145 (45), 2186 (280), 2217 (22), 2872 (10), 2908 (25 br), 2961 (12), 2978 (30), 3012 (52), 3101 (30).

4. Triethoxyvinylethynylsilane cm^{-1}: 590 (12), 685 (3), 714 (16 br), 794 (8 br), 932 (10), 1043 (3), 1089 (10 br), 1110 (15 br), 1290 (21), 1352 (5), 1410 (32), 1448 (10), 1595 (67), 2154 (160), 2217 (10), 2867 (20 br), 2882 (30), 2930 (52), 2978 (44), 3014 (35), 3100 (20).

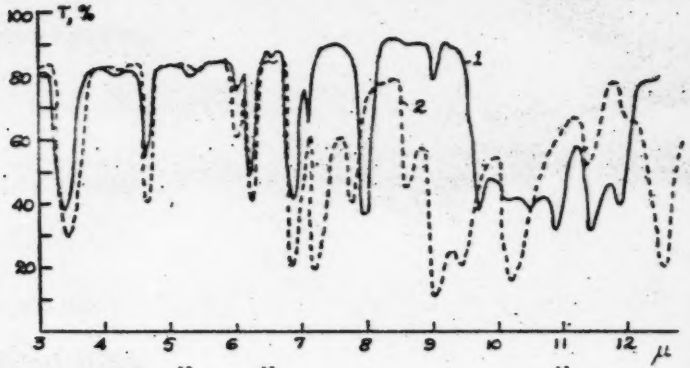
The Raman spectra were obtained with the ISP-51 apparatus, using the usual technique [6] for measurement of frequencies and intensities. The intensity of the 802 cm^{-1} frequency of cyclohexane was assumed to be 250 units. The measurements of the intensities were accurate to 15%, those of frequencies were accurate to ± 1 cm^{-1} for narrow lines and ± 3 cm^{-1} for broad or very weak lines. The infrared absorption spectra were obtained with an IKS spectrograph using a sodium chloride prism. The measurements of the bands at their minimum were accurate to ± 10 cm^{-1}. Examination of the spectra revealed a number of characteristic frequencies which are detailed in Table 4. The intensities of the frequencies are converted to the basis of identical numbers of molecules in the scattering volume.

TABLE 4
Characteristic Frequencies of the $\equiv Si-C\equiv C-CH=CH_2$ Radical

Substance	Frequencies in cm^{-1}, intensities per mole								
$(C_2H_5)_3SiC\equiv C-CH=CH_2$	1110 (24)	1290 (40)	1353 (5)	1410 (73)	1595 (61)	1611 (112)	2154 (340)	2217 (24)	3015 (68)	3105 (37)
$(C_2H_5)(CH_3)Si(H)-C\equiv C-CH=CH_2$	1110 (25)	1290 (32)	1357 (7)	1410 (62)	1595 (73)	1611 (73)	2154 (310)	2217 (19)	3015 (69)	3104 (3)
$CH_3HSi(C\equiv C-CH=CH_2)_2$	1110 (38)	1280 (42)	1352 (7)		1595 (115)	1611 (45)	2156 (380)	2217 (30)	3014 (70)	3101 (40)
$(C_2H_5O)_3Si-C\equiv C-CH=CH_2$	1110 (27)	1290 (38)	1352 (9)	1410 (58)	1595 (120)	–	2154 (290)	2217 (18)	3014 (63)	3100 (36)



1) $(C_2H_5)_3SiC\equiv C-\overset{H}{\underset{|}{C}}=CH_2$; 2) $CH_3Si(C\equiv C-\overset{H}{\underset{|}{C}}=CH_2)_2$



1) $(CH_3)(C_2H_5)SiC\equiv C-\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}=CH_2$; 2) $(C_2H_5O)_3SiC\equiv C-\overset{H}{\underset{|}{C}}=CH_2$

The frequencies set forth may serve as an analytical characteristic of the vinylethynyl radical. Attention may be drawn to the position of the frequencies of the C=C linkage at 2154 cm^{-1} and 2217 cm^{-1} and of the C=C linkage at 1596 and 1611 cm^{-1}, to the valence vibrations in the $=CH_2$ group at 3015 and 3104 cm^{-1}, and to the deformation vibrations in the $-CH=CH_2$ group at 1290, 1353, and 1410 cm^{-1} [7,8]. A striking feature is the absence of characteristic regularities of intensities, evidently due to strong interaction of the electronic clouds at the frequencies of the triple and double conjugated linkages in opposition to the allylsilanes. Similar analytically characteristic bands in the infrared spectrum have the values of 4, 6, 6.0, 6.2, 6.9, and 9.0 μ.

This investigation enabled us to solve diverse problems of the determination of the structure of derivatives of vinylethynylsilanes. We give some examples. The addition of bromine to the triple bond of vinylethynylsilanes was confirmed by the infrared spectra, the absence from which of bands in the 4 μ region in association with the presence of a band at 6.15 μ being characteristic of the C=C bond.

The spectra of acetylenic hydrocarbons (evaluated below) invariably showed the frequency of the triple bond in the α-position to be 2175 cm^{-1}, which enabled the determination in the spectrum of the above-mentioned product

of selective hydrogenation of vinylethynylsilane (butadienylsilane) of contamination with both the starting material (frequency 2154 cm^{-1}, 1595 cm^{-1}, 1611 cm^{-1}), and trialkyl-1-butynesilane (frequency 2175 cm^{-1}); it also gave confirmation of the presence of a conjugated double bond (frequency 1625 cm^{-1}). In the spectrum of the second product of hydrogenation of triethylbuten-2-silane was found a frequency of 1656 cm^{-1}, which confirmed the position of the double bond; evidence for this position is also the absence from the spectrum of the frequencies of the $-CH_2$ group (3000 cm^{-1}, 3075 cm^{-1}), etc.

Of the chemical reactions of vinylethynylsilanes, especially interesting were the addition reactions which enabled transition from silicohydrocarbons and other compounds of the enynic series to compounds of the butadiene series and also two acetylenic silicohydrocarbons with one and two atoms of silicon. We have already mentioned above that two atoms of bromine add on at the triple bond and two atoms at the double bond. The tribromide of triethylvinylethynylsilane [$(C_2H_5)_3SiCBr{=}CBrCHBr{=}CH_2$ with b.p. 170–172° (11 mm); n_D^{20} 1.5889 and d_4^{20} 1.5605] that we prepared proved to be very stable; it did not decompose when kept for many weeks and it slowly polymerized. The stability of the dibromide of vinylethynylsilane prompted us to attempt the addition of gaseous HCl to trimethylvinylethynylsilane at −70°. In these conditions the HCl does not rupture the Si–C linkage so that we were able to obtain a stable dichloride structurally analogous (I) or identical (II) (in the case of addition of a second molecule of HCl in the 1–4 position) with the dichloride which is formed by addition of two moles of HCl to 1-buten-3-yne:

$$\gtrless Si-CH{=}C\cdot Cl-CH_2-CH_2\cdot Cl \quad (I) \qquad \gtrless Si-CH_2-C\cdot Cl{=}CH-CH_2\cdot Cl. \quad (II)$$

Physical properties of the dichloride: b.p. 105-107 (52 mm); n_D^{20} 1.4738; d_4^{20} 1.0092.

A study was also made of the reaction of butyllithium with triethylvinylethynylsilane. The reaction proceeded violently with heat evolution (it was necessary to cool the flask); a bluish-green organometallic compound was formed. After treatment with acidified water, the reaction product was dried and fractionally distilled to give 2 fractions:

Fr. I, b.p. 93 – 94° (3 mm); d_4^{20} 0.8118; n_D^{20} 1.4560
Fr. II, b.p. 174 – 176° (3 mm); d_4^{20} 0.8482; n_D^{20} 1.4769
Residue: an oily liquid

Fraction I gave the following Raman spectrum: 447 (2), 569 (5 br) 606 (4), 720 (4 br), 803 (4), 963 (3 br), 1013 (4 br), 1082 (2 br), 1116 (4), 1231 (4 br), 1306 (2), 1326 (3), 1374 (3), 1413 (4), 1435 (4), 1462 (6), 2175 (10).

Of these frequencies, that of 2175 (10) belongs to the triple bond in the α-position to the silicon; there are no double bonds in the spectrum. From Stepanov's work [9] we know that simple branching (tertiary carbon atom −CH−) is characterized by frequencies of 1140 cm^{-1} and 1170 cm^{-1}; on the other hand, Egorov and Bazhulin [8] report spectra of β-allylpropyltrimethylsilane and β-allylpropyltriethylsilane which actually contain the frequencies of 1129 (2) and 1155 (4) and which must evidently be attributed to simple branchings of the molecules in question. The spectrum of fraction I with b.p. 93 – 94° (3 mm) does not contain any of these frequencies and consequently we can assume that fraction I is triethyl-1-octynesilane, formed according to the scheme:

$$(C_2H_5)_3Si-C{\equiv}C-CH{=}CH_2 + LiC_4H_9 \longrightarrow (C_2H_5)_3Si-C{\equiv}C-\underset{\displaystyle Li}{\underset{|}{CH}}-CH_2\cdot C_4H_9 \xrightarrow{H_2O} (C_2H_5)_3Si-C{\equiv}C-CH_2-CH_2-C_4H_9.$$

In Table 5 are set forth the analytical data for triethyl-1-octynesilane.

Originally we suggested that the fraction with b.p. 174 – 176° (3 mm) was the result of addition of 2 moles of C_4H_9Li according to the scheme:

$$(C_2H_5)_3Si-C{\equiv}C-CH{=}CH_2 + 2C_4H_9Li \longrightarrow (C_2H_5)_3Si-\underset{\displaystyle Li}{\underset{|}{C}}{=}\underset{\displaystyle C_4H_9}{\underset{|}{C}}-\underset{\displaystyle Li}{\underset{|}{CH}}-CH_2\cdot C_4H_9 \xrightarrow{H_2O} (C_2H_5)_3Si-CH{=}\underset{\displaystyle C_4H_9}{\underset{|}{C}}-CH_2-CH_2\cdot C_4H_9,$$

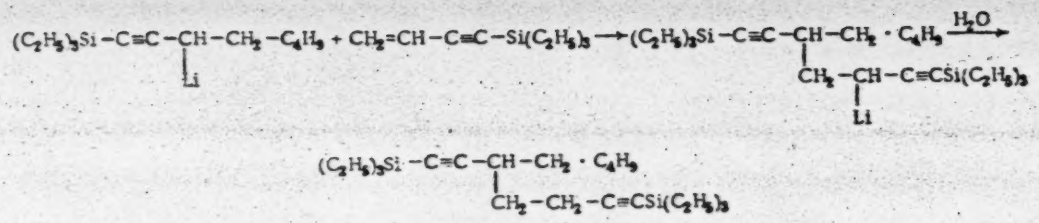
i.e. a product with the composition $C_{18}H_{38}Si$. The infrared spectrum of this fraction and its elementary analysis, however, did not confirm this suggestion.

In the spectrum was detected an intense absorption band at about 4.6μ which was unequivocal evidence of the presence of the C≡C linkage. The Raman spectrum in turn exhibited the stable C≡C frequency of 2175 cm^{-1} and did not contain the frequencies in the 1600 cm^{-1} region which are characteristic of the double bond. The elementary composition of this fraction corresponded to the formula $C_{24}H_{46}Si_2$, i.e. to a diacetylenic disilane apparently formed by interaction of the alkynyllithium with the original vinylethynylsilane according to the scheme:

TABLE 5

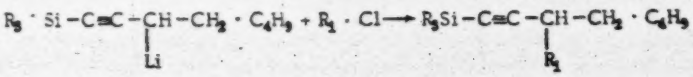
Properties of Acetylenic Mono- and Disilanes and of Diacetylenic Di- and Trisilanes

Substance	B.p. in °C (p in mm mercury)	d_4^{20}	n_D^{20}	MR found	MR calculated	Found % C	Found % H	Found % Si	Calculated % C	Calculated % H	Calculated % Si
Triethyl-1-octynesilane $(C_2H_5)_3Si-C\equiv C-CH_2\cdot CH_2\cdot C_4H_9$	93.5-94 (3)	0.8118	1.4560	75.14	74.97	74.98	12.62	12.37	74.92	12.57	12.51
Triethylisododecynesilane $(C_2H_5)_3Si-C\equiv C-\underset{\displaystyle C_2H_5}{\underset{\vert}{CH}}-CH_2-C_4H_9$	98-99 (3)	0.8069	1.4520	84.40	84.23	76.01	12.62	11.27	76.11	12.77	11.11
Triethyl-(γ-trimethylsilyl-δ-butyl)-vinylethynylsilane $(C_2H_5)_3Si-C\equiv C-\underset{\displaystyle Si(CH_3)_3}{\underset{\vert}{CH}}-CH_2C_4H_9$	108-109.5 (3)	0.8180	1.4555	98.44	98.49	69.56	12.39	16.96	68.87	12.22	18.92
Trimethyl-1-pentynesilane $(CH_3)_3Si-C\equiv C-CH_2-CH_2\cdot CH_3$	65-67 (52)	0.7597	1.4263	47.34	46.89	68.46	11.59	18.78	68.49	11.50	20.00
Triethyl-(γ-triethylsilylbutynyl-δ-butyl)-vinylethynylsilane $(C_2H_5)_3Si-C\equiv C-\underset{\displaystyle CH_2\cdot C_4H_9}{\underset{\vert}{CH}}-CH_2-CH_2-C\equiv CSi(C_2H_5)_3$	174-176 (3)	0.8482	1.4769	129.90	129.29	73.77	11.78	14.43	73.77	11.87	14.36
The diacetylenic trisilane $(C_2H_5)_3Si-C\equiv C-\underset{\displaystyle CH_2\cdot C_4H_9}{\underset{\vert}{CH}}-CH_2-\underset{\displaystyle Si(CH_3)_3}{\underset{\vert}{CH}}-C\equiv C\cdot Si(C_2H_5)_3$	255-258 (3)	0.8739	1.4880	207.30	207.13	71.26	11.53	17.28	70.06	11.76	18.18
The diacetylenic disilane $(C_2H_5)_3Si-C\equiv C-\underset{\displaystyle CH_2\cdot C_4H_9}{\underset{\vert}{CH}}-CH_2-\underset{\displaystyle C_2H_5}{\underset{\vert}{CH}}-C\equiv C-Si(C_2H_5)_3$	181-182 (4)	0.8424	1.4720	139.10	138.6	74.17	11.96	13.69	74.5	12.03	13.47

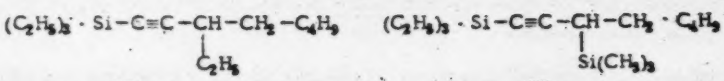


The analytical data of this fraction are set forth in Table 5.

We may note that the above-mentioned alkynyllithium readily condensed both with alkyl halides and with trialkyl-halogenosilanes according to the general scheme:



a secondary product being the above-noted diacetylenic disilane. In this manner we synthesized the monosilane (V) and the disilane (VI).

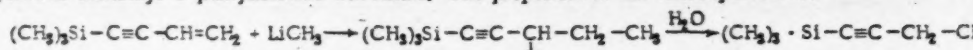


(V) (VI)

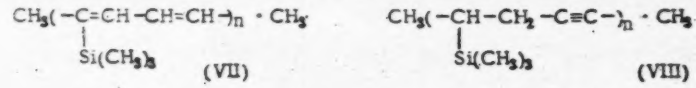
The properties and analytical data of these compounds are set forth in Table 5. Disilane (VI) is a representative of the unsymmetrical acetylenic disilanes similar in structure to the symmetrical disilanes which were recently synthesized by Petrov and Shchukovskaya [10] and simultaneously by Frisch and Joung [5] by condensation of trialkyl-halodisilanes with the symmetrical complex of lotsich.

The above-mentioned lithium derivative was subjected not only to hydrolysis but also to alkylation with both C_2H_5Br and $Cl \cdot Si(CH_3)_3$; the resultant disilane and trisilane are included in Table 5.

Apart from the addition to vinylethynylsilanes of butyllithium, the addition of methyllithium to trimethyl-vinylethynylsilane was investigated. The product of the reaction was likewise hydrolyzed and fractionally distilled. The yield of trimethyl-1-pentynesilane was small. The properties of this silicohydrocarbon



(the fourth conpound listed in Table 5) were similar to those of the silicohydrocarbon recently synthesized by another route by Frisch and Joung [5]. Distillation of this silicohydrocarbon did not yield any higher fractions such as were observed in the case of addition of butyllithium, while the main product of the reaction (the "residue") very quickly changed into an oxygen-containing, sticky polymer with a yellowish-brown color. This poylmer, soluble in organic solvents and fusible, must evidently be assigned the structure of (VII) or (VIII):



(VII) (VIII)

SUMMARY

1. It was shown that vinylethynylmagnesium halide condenses in high yield with both trialkyl-halogenosilanes and with aryldialkyl-halogenosilanes, monoalkyl-halogenosilanes, and even withsilicon tetrachloride.

2. All the vinylethynylsilanes, and with particular ease divinylethynylsilanes, polymerize spontaneously on standing in the air to form transparent, peroxide-containing resins. Vinylethynylsilanes are capable, however, of polymerizing even in absence of air when heated in sealed tubes to 100°.

3. The velocities of polymerization of the vinylethynylsilanes were correlated with their structure. In the trialkylvinylethynylsilanes the rate of polymerization rises with increasing length of radical from methyl through butyl. In the dimethylarylsilane series it falls from phenyl to benzyl and from α-naphthyl to p-tolyl.

4. Selective hydrogenation of triethylvinylethynylsilane gave triethylbutadienylsilane and triethylbuten-2-silane.

5. In the bromination of vinylethynylsilanes the first two atoms of bromine add on at the triple bond, leading to polymerizable derivatives of the butadiene type. HCl at −70° also adds on but in the proportion of two molecules, forming a dichloride structurally analogous to that obtained by addition of 2 moles HCl to 1-buten-3-yne.

6. In contrast to hydrogen, bromine and hydrogen halides, which first add on at the triple bond, alkyllithiums only add on at the double bond of the enyne grouping. The resultant alkynyllithiums can be hydrolyzed by water or alkylated by alkyl halides to form silicohydrocarbons of the acetylenic series; their alkylation with trialkylhalogenosilanes gives unsymmetrical acetylenic disilanes. Diacetylenic disilanes are got from the alkynyllithium (via addition of butyllithium).

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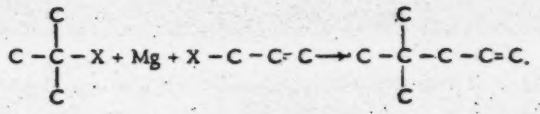
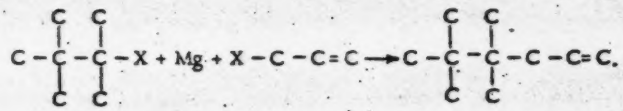
SYNTHESIS OF PARAFFINIC HYDROCARBONS WITH TWO ADJACENT QUATERNARY CARBONS

A. D. Petrov and L. I. Lavrishcheva

Organomagnesium synthesis of pure paraffinic hydrocarbons containing two adjacent quaternary carbons is a matter of considerable difficulty [1]. Whereas condensation according to reaction (1) proceeds with a yield of 85%, that according to reaction (2) proceeds with a yield of only 4%.

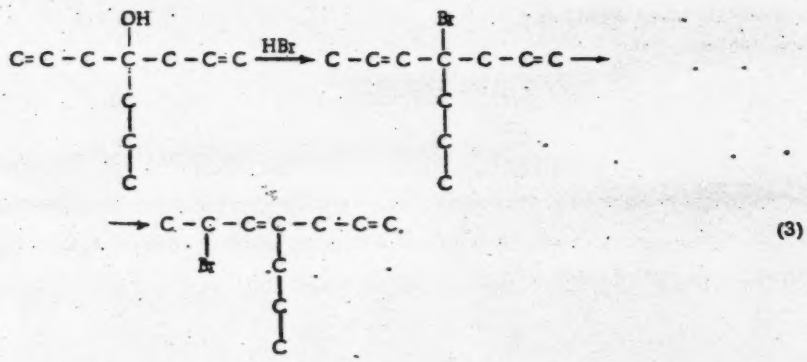


(1)



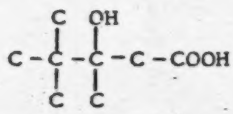
(2)

Since it is immaterial for the purpose of synthesis whether the double bond which activates the condensation is at the primary or tertiary halogen, it was decided to study the behavior in this reaction of unsaturated tertiary halides of various structures. It was found that whereas in the synthesis of the halohydrin from dimethylallylcarbinol there was scarcely any isomerization of the allyl radical into propenyl and the resultant halide containing a double bond in the γ-position proved incapable of entering into condensation, the preparation of the bromohydrin from diallylpropyl carbinol was accompanied by translocation of the double bond into the β-position in one of the allyl radicals. This rendered the halide active, but simultaneously, due to the allylic rearrangement, the halide structure was altered:

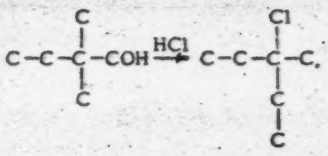


(3)

Instead of 4-bromo-4-propyl-1,5-heptadiene, there was formed 4-propyl-6-bromo-1,4-heptadiene, the condensation of which had previously failed to give a quaternary carbon [2]. This difference in behavior of tertiary alcohols of differing structures containing allyl radicals toward hydrogen halides led us to search for tertiary alcohols, containing allyl radicals, the formation from which of halohydrins would proceed with migration of the double bond to the β-position but without the accompaniment of the allylic rearrangement. Such an alcohol was found in methyl-tert-butylallylcarbinol which proved to be a convenient starting material for the synthesis of hydrocarbons containing two quaternary carbons. Methyl-tert-butylallylcarbinol was first prepared by Gnedin [3] who also established its structure by oxidizing it to the hydroxy acid:



In the preparation of the chlorohydrin from methyl-tert-butylallylcarbinol, we made use of the observations of Favorsky [4] and Whitmore [5] who showed that primary and secondary branched alcohols of the type of tert-R–COH and tert-R–C–OH undergo rearrangement on substitution of the hydroxyl group by halogen and are transformed into
R_1
tertiary halides:



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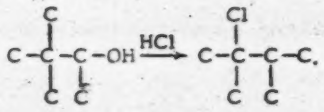
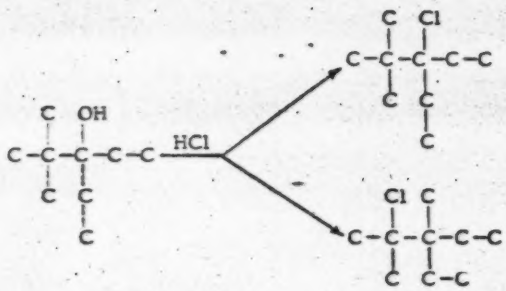


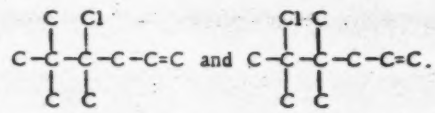
(5)

We also took into consideration the results of Brown and Fletcher [6] who observed a similar rearrangement of tertiary alcohols:



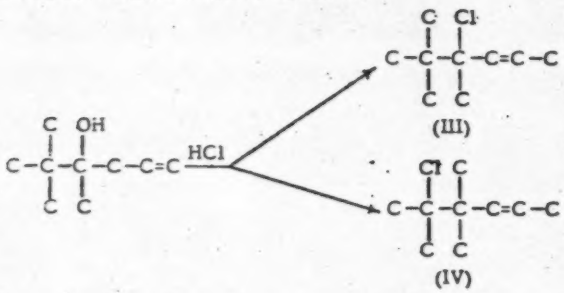
(6)

The behavior of branched olefinic alcohols had not previously been investigated; by analogy with the above-cited facts we thought that we might here also be able to obtain two chlorides:



(I) (II)

Moreover, allowing for the possibility of translocation of the double bond from the γ- to the β-position, the following general reaction scheme could be advanced:

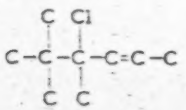


(III)

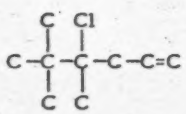
(IV)

Oxidation of the chloride with 1% aqueous $KMnO_4$ gave the following products: α, β, β-trimethyl-α-hydroxybutyric acid, β, β-dimethyl-α-oxobutyric acid, acetic acid, formic acid and much smaller amounts of pinacolone and oxalic acid. The products of oxidation exclude the presence of the chloride (IV) because we failed to detect α, α, β-trimethyl-β-hydroxybutyric acid and dimethylacetoacetic acid.

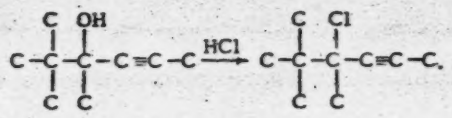
Consequently the chloride must be assigned the structure:



with a small admixture of

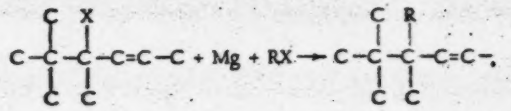


It should be mentioned that Zakharova [7] and Favorskaya [8] studied the interaction of acetylenic alcohols of similar structure with hydrochloric acid; investigation of the structure of the halohydrins showed that they do not suffer rearrangement and give only one chloride:



(7)

Reaction of the chloride prepared by us with RMgX enabled the synthesis of hydrocarbons containing two adjacent quaternary carbon atoms according to the scheme:



(8)

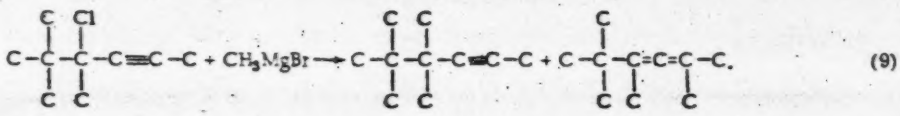
where R is allyl and propyl.

TABLE

Reaction of chlorides C	Yields of products		
	of cleavage $HX-C_9H_{16}$ in %	of condensation	of dimerization $C_{18}H_{34}$
(I) CH_3I	36	–	16%
(II) C_3H_5Br	20	30% $C_{12}H_{22}$	not detected
(III) C_3H_7Br	30	23% $C_{12}H_{24}$	5%

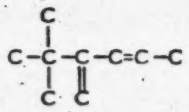
The product of reaction of the chloride with CH_3I could not be isolated in the pure form since the above reaction was accompanied by side reactions: cleavage of HCl and dimerization of the original allyl halide. The results of the reaction are set forth in the table.

Reaction (8) has the advantage over the similar reaction of Zakharova and Sapozhnikova [9] that it yields one hydrocarbon and not a mixture of acetylenic and allenic hydrocarbons:

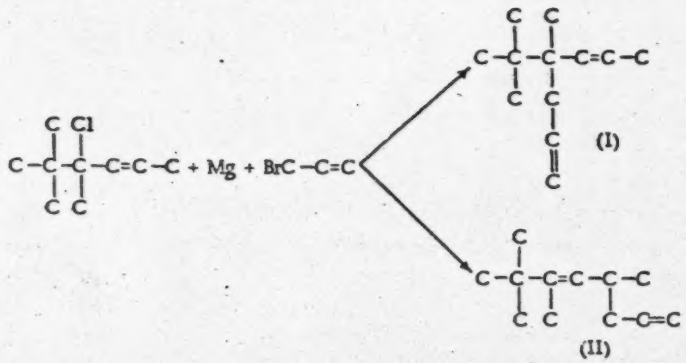


(9)

Oxidation of the hydrocarbon C_9H_{16} gave β, β-dimethyl-α-oxobutyric, acetic and formic acids; hence it can be assigned the structure:



Oxidation of $C_{12}H_{22}$ gave a dibasic acid $C_9H_{26}O_4$, formic and acetic acids, as well as an insignificant amount of β, β-dimethyl-α-oxobutyric acid. We also suggested the possibility of formation of pinacolone and of methylsuccinic acid which should have been obtained if the allyl halide rearranged from tertiary to secondary:



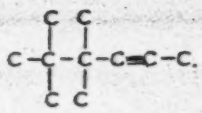
(I)

(II)

(10)

The results of oxidation showed, however, that the reaction only proceeds according to the first scheme.

It should be noted that oxidation of the hydrocarbon $C_{12}H_{24}$ obtained by reaction with C_3H_7MgBr proceeds with extraordinary difficulty. Here again we may draw a comparison with the acetylenic hydrocarbon obtained by Zakharova [9]:



Oxidation of $C_{12}H_{24}$ was effected with 2, 4 and 6% $KMnO_4$ and each time only 20-25% of the charge of hydrocarbon was oxidized, the remainder being recovered unchanged. The oxidation yielded a monobasic acid $C_{10}H_{20}O_2$ and traces of 2, 3-dimethyl-α-oxobutyric acid. Pinacolone and α-methylvaleric acid (products which should have been formed by rearrangement) were not detected.

EXPERIMENTAL

Synthesis of methylallyl-tert-butylcarbinol. To 92 g (3.8 moles) Mg in 1 l ether was added in the course of 14 hours a mixture of 260 g allyl chloride and 201 g pinacolone. The mixture was boiled for 8 hours and was decomposed with iced water and 10% HCl. Yield 219 g (77% of the theoretical) of alcohol with b.p. 168-172°; n_D^{20} 1.4452. Literature data [3]: b.p. 168.4°; n_D^{20} 1.4476; d_4^{20} 0.85508 and b.p. 169.5-170°; n_D^{20} 1.4452; d_4^{20} 0.8553.

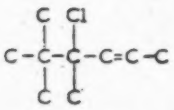
Hydrochlorination of 2, 2, 3-trimethyl-5-hexen-3-ol. 247 g alcohol was saturated with dry HCl in presence of Na_2SO_4 at 0-3°. Yield 216 g chloride in a yield of 80%. The chloride (here prepared for the first time) had the constants: b.p. 46-47° (6 mm); n_D^{20} 1.4575; d_4^{20} 0.9101.

	Found %: Cl 22.3; 21.7
$C_9H_{17}Cl$.	Calculated %: Cl 22.06

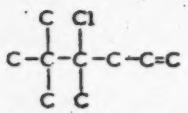
Oxidation of the chloride. 15 g chloride was emulsified in 400 ml water and addition was made of 5 g KOH and (portionwise) 44 g $KMnO_4$. The neutral products of oxidation were distilled off with steam into a solution of 2,4-dinitrophenylhydrazine. Yield about 0.3 g pinacolone derivative with m.p. 124-125°. A mixed sample did not give a depression of m.p. After separating the MnO_2, the solution of salts of the acids was evaporated and decomposed with 20% H_2SO_4, the organic acids were extracted with ether. In all 4.5 g acids was obtained; from this was isolated 0.2 g oxalic acid with m.p. 99-100°, not giving a depression in the mixed melting test. Separation of the oxalic acid was followed by precipitation of crystals with m.p. 84-88°; subsequent recrystallizations from chloroform gave m.p. 141-142°, corresponding to α,β,β-trimethyl-, α-hydroxybutyric acid which did not give a depression of melting point in admixture with an authentic specimen. The acid for the mixed melting test was obtained by oxidation of 2,2,3,6,7,7-hexamethyl-3,6-diol-4-octyne [10]. The mother liquor, after separation of the crystals, was treated with 2,4-dinitrophenylhydrazine to give 1 g hydrazone which after recrystallization from alcohol had m.p. 171-172°.

	Found %: N 18.09; 18.14
$C_{12}H_{14}N_4O_8$.	Calculated %: N 18.06

The nitrogen content and the melting point of this compound correspond to the 2,4-dinitrophenylhydrazone of β,β-dimethyl-α-oxobutyric acid. The acid for the mixed melting test was obtained by Glucksman's method [11] of oxidation of pinacolone, and the 2,4-dinitrodiphenylhydrazone was prepared for the first time with m.p. 171-172°. The mixed melting test with the 2,4-dinitrophenylhydrazone of the product of oxidation of the hydrocarbon did not show a depression of m.p. Consequently the chloride has the structure



and contains an insignificant amount of



Reaction of the chloride with CH_3MgI. To 24 g Mg was added a mixture of 118 g (0.8 mole) CH_3I and 64 g (0.4 mole) chloride in the course of 4 hours while cooling with iced water. The mixture was heated for 10 hours at 40°. After working up in the usual manner and distillation over sodium in a column with an efficiency of 15 theoretical plates, the following were obtained:

Fraction I with b.p. 126-129°; 17.7 g; n_D^{20} 1.4275; d_4^{20} 0.7510; found MR 42.61; calculated for $C_9H_{16}F_2$ MR 42.98. This is the product of cleavage of hydrochloric acid from the chloride. From fraction II 8 g (with b.p. 138-158°) was separated after several distillations a 2 g fraction with b.p. 157-158°; n_D^{20} 1.4330; d_4^{20} 0.7604; found MR 47.74; calculated for $C_{10}H_{20}F_2$ MR 47.91.

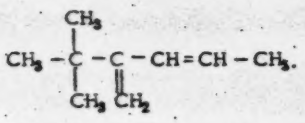
	Found %: C 85.80; H 14.20
$C_{10}H_{22}$.	Calculated %: C 85.62; H 14.38

Fraction III with b.p. 254-260° was obtained in a yield of 8.3 g; n_D^{20} 1.4615; d_4^{20} 0.8128. The structure of the hydrocarbons present in this fraction was not investigated.

Oxidation of C_9H_{16}. 10.8 g hydrocarbon was oxidized with 1% $KMnO_4$. A total of 52 g $KMnO_4$ was added instead of the calculated 65 g. Among the water-soluble acids were identified formic acid (by the calomel test) and acetic acid; the water-insoluble acid was separated in the form of the silver salt.

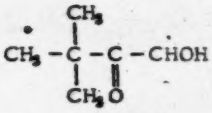
	Found %:	Ag 46.26
$C_6H_9O_3Ag$.	Calculated %:	Ag 45.5

The water-insoluble acid gave a 2,4-dinitrophenylhydrazone with m.p. 171-172°. These data identify the water-insoluble acid as β,β-dimethyl-α-oxobutyric acid and permit the diolefin to be assigned the following structure:



In addition to the acid a neutral product of oxidation was isolated: crystals with a camphor odor, m.p. 51°.

	Found %:	C 66.72; 66.70; H 11.57; 11.75
$C_9H_{16}O_2$.	Calculated %:	C 66.63; H 11.18

This is probably the ketoalcohol  , formed by oxidation of the tertiary bond.

Reaction of chloride with allyl bromide. A mixture of 106.5 g (2.3 moles) chloride and 136 g (1.12 moles) allyl bromide was added in the course of 11 hours to 48 g Mg. The mixture was then heated 10 hours at 40°. Working-up in the usual manner and fractionation in a column gave: 2-tert-butyl-1,3-pentadiene, 17 g, yield 20.6%; hydrocarbon of composition $C_{12}H_{22}$ 31.5 g, yield 28%; b.p. 176.5-178.5°; n_D^{20} 1.4420; d_4^{20} 0.7712; found MR 57.05; for $C_{12}H_{22}F_2$: calculated MR 56.68; found bromine number 201 and 200; calculated for $C_{12}H_{22}$ 193.

	Found %:	C 86.92; 86.80; H 13.20; 13.10
$C_{12}H_{22}$.	Calculated %:	C 86.66; H 13.34

2,2,3-Trimethyl-3-propylhexane was obtained by hydrogenation of $C_{12}H_{22}$ over nickel: b.p. 191-193° (756 mm); n_D^{20} 1.4310; d_4^{20} 0.7654; found MR 57.59; calculated for $C_{12}H_{26}$ MR 51.62.

	Found %:	C 84.86; 85.04; H 14.76; 14.94
$C_{12}H_{26}$.	Calculated %:	C 84.61; H 15.39

The solidifying temperature of 2,2,3-trimethyl-3-propylhexane was below −70°. In the case of the close (but less asymmetrical) structural analog 2,2,3,3,-tetramethylhexane the solidifying temperature is −54° [12].

Oxidation of $C_{12}H_{22}$. 10 g hydrocarbon was oxidized with 2% $KMnO_4$ solution. No neutral products of oxidation were isolated. Formic and acetic acids were identified among the acidic products, also a fraction of high-molecular acids with b.p. 140-150° (5 mm), consisting of structurally similar dibasic acids of the composition $C_9H_{16}O_4$ and $C_{10}H_{18}O_4$ with a trace of β,β-dimethyl-α-oxobutyric acid. The presence of the latter, due to contamination with hydrocarbon C_9, was evidenced by the too-low content of silver and also by formation of a 2,4-dinitrophenylhydrazone with m.p. 171°.

	Found %:	Ag 51.25
$C_9H_{14}O_4Ag_2$.	Calculated %:	Ag 53.5
$C_{10}H_{16}O_4Ag_2$.	Calculated %:	Ag 51.6
$C_6H_9O_3Ag$.	Calculated %:	Ag 45.5

Reaction of chloride with C_2H_5MgCl. To 24 g Mg in 250 ml ether is added, over a period of 6 hours, a mixture of 134 g (1.1 moles) propyl bromide and 80.3 g (0.5 mole) of the chloride $C_9H_{17}Cl$. The mixture is heated at 35° for 7 hours. The usual working-up and distillation over sodium gave: 1) 19 g C_9H_{16}, yield 30%; b.p. 126-128°; n_D^{20} 1.4262; d_4^{20} 0.7515.

	Found %:	C 86.87; 86.85; H 12.93; 12.85
C_9H_{16}.	Calculated %:	C 87.01; H 12.99

2) 20 g $C_{12}H_{24}$; yield 23%; b.p. 177-179°; n_D^{20} 1.4328; d_4^{20} 0.7594; found MR 57.57; calculated for $C_{12}H_{24}$ MR 57.15.

MR 57.15.

Found %: C 85.39; H 14.49; 14.51

$C_{12}H_{24}$. Calculated %: C 85.62; H 14.38

3) 3.2 g hydrocarbon with b.p. 250-260°; n_D^{20} 1.4610; d_4^{20} 0.8160; found MR 54.21; calculated for $C_{12}H_{24}F_2$ MR 54.39.

Oxidation of $C_{12}H_{24}$. 10.5 g hydrocarbon was oxidized with 2% $KMnO_4$ solution. Oxidation proceeded very slowly and was continued for 8 days. Only acidic products were isolated; they were fractionated in the form of silver salts:

	Weight of salt in g	Ag, in g	Ag in %
Fraction I	0.0747	0.0297	39.76
Fraction II	0.0508	0.0254	50.0

$C_{10}H_{19}O_2$. Calculated % Ag 38.65

Fraction I corresponds to a monobasic acid with the composition C_{10}. Fraction II is apparently a mixture of acetic and β,β-dimethyl-α-oxobutyric acids, the latter originating from the presence of hydrocarbon C_9 formed by cleavage of HCl from the chloride.

SUMMARY

1. It was established that the tertiary halide of the alcohol synthesized from pinacolone and MgBrC – C≡C, is an active halide with a double bond in the β-position which reacts with RMgX in the tertiary form; the latter does not undergo the allyl rearrangement.

2. This characteristic of the halide in question, which differentiates it from the halide of dimethylallylcarbinol (in whose formation translocation of the double bond does not occur) and from other tertiary halides containing an allyl grouping which suffer the allylic rearrangement, enabled us to utilize the tertiary halide, 2-chloro-4, 5,5-trimethyl-2-hexene (prepared by us for the first time), in the synthesis of hydrocarbons containing two adjacent tertiary carbons.

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BRIEF COMMUNICATIONS

SYNTHESIS OF ARYL-β-CHLOROVINYL KETONES

A. N. Nesmeyanov, N. K. Kochetkov and M. I. Rybinskaya

The diverse reaction possibilities of β-chlorovinyl ketones, manifested by the high mobility of the chlorine atom, the activity of the double bond and the simultaneous substitution of the oxygen of the carbonyl group, make β-chlorovinyl ketones suitable starting materials for the synthesis of compounds of the most diverse classes [1]. It is therefore entirely natural that attempts should be made to broaden the possibilities of new methods of organic synthesis on the basis of β-chlorovinyl ketones by utilizing new representatives of the class of β-chlorovinyl ketones. Up to now the transformations of β-chlorovinyl ketones have been studied mainly with reference to alkyl-β-chlorovinyl ketones, whose synthesis we recently described [1]. In the present paper we describe the synthesis of aryl-β-chlorovinyl ketones, the reactions of which do not differ from those of their aliphatic analogs.

In the patent literature there is reference [2] to the possibility of obtaining phenyl-β-chlorovinyl ketone by condensation of benzoyl chloride with vinyl chloride in presence of aluminum chloride by the Kondakov-Krapivin reaction. Numerous repetitions of this synthesis in our laboratory led to negative results, and this lack of success is confirmed in the work of other authors [3]. Condensation of benzoyl chloride with vinyl chloride, conducted in various conditions, leads to a difficulty resolvable mixture of phenyl-β-chlorovinyl ketone and phenyl-β,β-dichloroethyl ketone from which the chlorovinyl ketone can only be isolated in low yield:

$$C_6H_5COCl + CH_2{=}CHCl \xrightarrow{AlCl_3} \begin{cases} \rightarrow C_6H_5COCH{=}CHCl \\ \rightarrow C_6H_5COCH_2CHCl_2 \end{cases}$$

Panizzi [3] used an old method of Claisen [4] for synthesis of phenyl-β-chlorovinyl ketone. Claisen obtained phenyl-β-chlorovinyl ketone by treating hydroxymethylene acetophenone with thionyl chloride [5] but he did not give a detailed account of his procedure. An exhaustive investigation of this reaction enabled us to establish the precise conditions for synthesis and to extend it to other hydroxymethylene ketones, so that we were able to develop a general method of synthesis of aryl-β-chlorovinyl ketones according to the scheme:

$$ArCOCH_3 \xrightarrow[Na]{HCOOC_2H_5} ArCOCH{=}CHONa \xrightarrow{SOCl_2} ArCOCH{=}CHCl.$$

It was found more convenient to isolate the sodium enolate of the hydroxymethylene ketone, to free it from unreacted substituted acetophenone by repeated washing with ether, and only after this treatment to bring it into reaction with thionyl chloride. In this manner we succeeded in obtaining aryl-β-chlorovinyl ketones in satisfactory yields. By this method, starting from acetophenone, p-tolylmethyl ketone, p-bromoacetophenone and p-methoxyacetophenone, we obtained (respectively) phenyl-, p-tolyl-, p-bromophenyl- and p-methoxyphenyl-β-chlorovinyl ketones in yields of 30-60%

These aryl-β-chlorovinyl ketones are high-boiling liquids or readily fusible solids (p-bromophenyl- and p-methoxyphenyl-β-chlorovinyl ketones), considerably more stable in storage than their aliphatic analogs. Their reactivity is apparently rather lower than that of the alkyl-β-chlorovinyl ketones, but the character of the chemical behavior itself is perfectly analogous, as we were able to show when using them for the synthesis of flavine salts: on the basis of p-methoxyphenyl-β-chlorovinyl ketone was obtained a natural anthocyanidin, while the methyl ether gave hesperidin [6].

EXPERIMENTAL

Phenyl-β-chlorovinyl ketone. To a suspension of 5.0 g finely pulverized sodium, 17.0 g ethyl formate and 100 ml absolute benzene were added dropwise, with energetic stirring and with cooling, 24.0 g acetophenone in

benzene (1:1). After 3 hours' stirring at room temperature, the precipitate of sodium salt of hydroxymethylene acetophenone was quickly filtered, washed with absolute ether, transferred again to the flask, covered with benzene and decomposed by cautious addition of water and then of 10% sulfuric acid. The benzene layer was dried over calcium chloride and filtered; then 26.0 g thionyl chloride was added and the mixture heated on a water bath until hydrogen chloride ceased to come off; this required about 5 hours. The benzene was distilled off and the residue distilled in vacuum to give 16.5 g (50% of the theoretical) of phenyl-β-chlorovinyl ketone with b.p. 118-120° (10 mm); n_D^{20} 1.5742. Literature data [4]: b.p. 125-127° (18 mm).

p-Tolyl-β-chlorovinyl ketone is similarly prepared from 50.0 g p-tolylmethyl ketone, 36.0 g ethyl formate, 10.0 g sodium in 200 ml benzene and 50.0 g thionyl chloride. Yield 24.0 g (30% of the theoretical) of substance with b.p. 118-120° (5 mm); n_D^{20} 1.5826; d_4^{20} 1.1680.

	Found %:	C 66.55; 66.29; H 5.23; 5.06
$C_{10}H_9OCl$.	Calculated %:	C 66.46; H 5.02

p-Bromophenyl-β-chlorovinyl ketone is similarly prepared from 40.0 g p-bromoacetophenone, 19.0 g ethyl formate, 4.6 g sodium in 150 ml benzene and 35 g thionyl chloride. The residue remaining after removal of the benzene crystallized. After recrystallization from ligroine, p-bromophenyl-β-chlorovinyl ketone forms fine needles with m.p. 38.5-39.5°; yield 19.0 g (40% of the theoretical).

	Found %:	C 43.88; 44.00; H 2.55; 2.42
C_9H_6OClBr.	Calculated %:	C 44.02; H 2.46

p-Methoxyphenyl-β-chlorovinyl ketone is prepared similarly from 16.0 g p-methoxyacetophenone, 16.0 g ethyl formate, 2.5 g sodium in 100 ml benzene and 30.0 g thionyl chloride. After vacuum distillation [b.p. 154-157° (3 mm)] the substance crystallized; recrystallization from ligroine gave lustrous needles with m.p. 47-48°; yield 12.5 g (60% of the theoretical).

	Found %:	C 61.17; 61.18; H 4.77; 4.72
$C_{10}H_9O_2Cl$.	Calculated %:	C 61.15; H 4.55

All the prepared aryl-β-chlorovinyl ketones are insoluble in water and readily soluble in common organic solvents.

Reaction of benzoyl chloride with vinyl chloride. Into a solution of 19.0 g benzoyl chloride in 50 ml dry carbon tetrachloride with energetic stirring and cooling with iced water is passed a stream of dry vinyl chloride and addition is made in small portions in the course of an hour of 30.0 g aluminum chloride. After 4 hours' passage of vinyl chloride, a violent reaction suddenly sets in and the mixture boils. After six hours' saturation with vinyl chloride, the mixture is poured onto ice, the lower layer is separated, the aqueous layer is extracted with chloroform, the extracts are dried with calcium chloride, the solvent is distilled off and the residue is distilled in vacuum. A fraction with b.p. 130-150° (10 mm) is collected and partly cyrstallizes on standing. Weight 15.0 g. Pure phenyl-β-chlorovinyl ketone could not be isolated from this fraction even after many distillations. Heating of the product with 10.0 g calcined potassium carbonate at 150-170° for 30 minutes gave, after working up in the usual manner, 5.1 g not perfectly pure phenyl-β-chlorovinyl ketone with b.p. 123-127° (10 mm).

SUMMARY

A method was developed for the synthesis of aryl-β-chlorovinyl ketone by condensation of substituted acetophenones with ethyl formate followed by treatment of the resultant hydroxymethylene ketone with thionyl chloride.

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THE ATOMIC REFRACTION OF PHOSPHORUS AND SULFUR IN POLYTHIOPHOSPHOORGANIC COMPOUNDS

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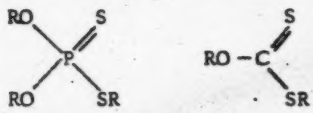
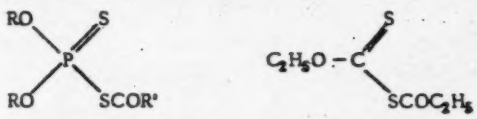
In a previous communication [1] we derived the values of the atomic refraction of phosphorus and sulfur in some thiophosphoorganic compounds. As we know, in esters, chloranhydrides and other derivatives of oxy acids of phosphorus the atomic refraction of phosphorus retains a constant value within a specific group of compounds [2]. Thus it is constant in derivatives of phosphoric acid (3.76 for the sodium D line), phosphorous acid (7.04), alkylphosphonic acids (4.27). Constancy of the atomic refraction of phosphorus in these compounds is manifested only when the character of the bond of the other elements with phosphorus is taken into account in the calculation. For example, for the chlorine atom it is necessary to assume a value of the atomic refraction characteristic of chlorine in chloroanhydride combination (6.336 derived from the molecular refraction of the haloanhydrides of carboxylic acids [3]), since the bond between chlorine and phosphorus bears the character of a haloanhydride bond. In derivatives of phosphoric acid the atomic refraction of the oxygen linked by a double (semi-polar) bond with phosphorus is equal to 2.211, as in ketones, and the carbonyl group of carboxylic acids. The literature contains many data for the thiophosphoorganic compounds. In a paper by Jones, Davies and Dyke [4] the value for the refraction of sulfur in thiophosphates is given as 9.68 (sodium D line).

Our study of the dialkylthiophosphites $(RO)_2PSH$ [5] has shown that the molecular refraction of compounds of this class can be calculated with satisfactory accuracy if a value of 9.70 is assumed for the atomic refraction of sulfur in accordance with the finding of Boudet and Rambaud [6] for thioketonic sulfur. In addition a study of the refraction of many representatives of the class of dialkyldithiophosphates $(RO)_2PSSH$, trialkyldithiophosphates $(RO)_2PSSR$ and mixed thioanhydrides of dialkyldithiophosphoric acid and carboxylic acids $(RO)_2PSSCOR'$ [1] showed that the refraction of the two sulfur atoms in these compounds was invariably equal to the refraction of the two sulfur atoms in purely carbon compounds possessing a similar structure. Thus, for trialkyldithiophosphates the group refraction for S_2 was found to be the same as that of esters of xanthic acid [7,6]:



$AR_{S_2} = 18.72$ $AR_{S_2} = 18.67 - 18.78$

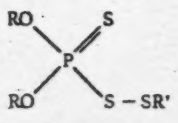
The refraction of the sulfur atoms in mixed anhydrides was also found to be equal to that in the corresponding purely carbon compound [8]:



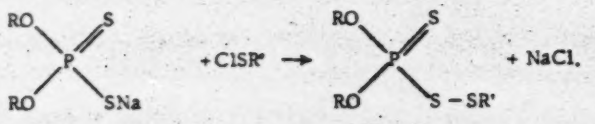
$AR_{S_2} = 19.77$ $AR_{S_2} = 19.53$

It appeared to be a matter of very great interest to establish whether the observed regularity is a general one. If this should be the case, then investigations in the field of phosphoorganic compounds would be considerably facilitated, and also there would be more opportunities for a comparative study of the problems of the reciprocal influence of atoms in phosphoorganic and in purely carbon compounds of the same type.

As a fresh object of investigation we chose the S-alkylthio-O,O-dialkylthiophosphates with the following structure:



The analogous purely carbon compounds are known. Thus, for methylthioacetyldisulfide $CH_3-C(=S)-S-SCH_3$ the group refraction of the three sulfur atoms, according to two authors is 27.68 [9] and 28.02 [6]. We realized the synthesis of the required S-alkylthio-O,O-dialkylthiophosphates by reaction of dialkyldithiophosphates of alkali metals with aliphatic sulfenyl chlorides [10]:



These are transparent liquids with a more or less deep-yellow color; they are soluble in carbon tetrachloride and benzene, insoluble in water; their constants are set forth in the table

TABLE 1

Formula	b.p. in °C (p in mm mercury)	Yield in %	n_D^{20}	d_4^{20}	MR	AR_{S_3}
$(C_2H_5O)_2PS_3CH_3$	100.5-101.5 (2.5)	41	1.5500	1.2142	60.93	27.49
$(i\text{-}C_3H_7O)_2PS_3CH_3$	99-100 (2)	60	1.5297	1.1471	70.09	27.42
$(C_2H_5O)_2PS_3C_2H_5$	106-107 (3)	39	1.5431	1.1810	65.76	27.68
$(i\text{-}C_3H_7O)_2PS_3C_2H_5$	117-118 (3.5)	48	1.5240	1.1189	75.05	27.75
$(C_2H_5O)_2PS_3C_4H_9$	139.5-140 (3.5)	30	1.5306	1.1246	75.33	28.03
$(i\text{-}C_4H_9O)PS_3C_2H_5$	129-130 (2.5)	22	1.5183	1.0866	84.39	27.85

The probable mean value of the group refraction for the three sulfur atoms was calculated from the data in the tables; it is equal to 27.70 ± 0.15.

Consequently even for such complex compounds as the investigated S-alkylthio-O,O-dialkyldithiophosphates, the value of the atomic refraction of the atoms linked to phosphorus is, within the limits of experimental error, equal to that in purely carbon compounds of the corresponding type.

EXPERIMENTAL

Preparation of S-alkylthio-O,O-dialkyldithiophosphates. The alkylsulfenyl chlorides were prepared by the patented method [10]. To the sodium or potassium dialkyldithiophosphate in a small quantity of carbon tetrachloride, with stirring and cooling to 10-5°, was added from a dropping funnel the equivalent amount of alkylsulfenyl chloride in carbon tetrachloride solution. Usually the alkylsulfenyl chloride at once entered into reaction, as marked by the disappearance of the bright-orange color. The reaction was later completed by heating the mixture on a water-bath at 50-60° for 2 hours. After cooling, the precipitate was filtered and the filtrate fractionated in vacuum. Yield of S-alkylthio-O,O-dialkyldithiophosphates from 10 to 20%.

S-Methylthio-O,O-diethyldithiophosphate was prepared from 6.72 g (0.03 mole) potassium diethyldithiophosphate and 2.35 g (0.025 mole) methylsulfenyl chloride. B. p. 100.5-101.5° (2.5 mm); n_D^{20} 1.5500; d_4^{20} 1.2142; yield 2.45 g (41% of theoretical).

	Found %:	P 13.41; 13.21	Found MR 60.93
$C_5H_{13}O_2PS_3$.	Calculated %:	P 13.36	Calculated MR 61.14*

S-Methylthio-O,O-diisopropyldithiophosphate was prepared from 5.9 g (0.025 mole) sodium diisopropyldithiophosphate and 2.35 g (0.025 mole) methylsulfenyl chloride. B.p. 99-100° (2 mm); n_D^{20} 1.5297; d_4^{20} 1.1471; yield 3.5 g (60% of the theoretical).

	Found %:	P 11.96; 11.93	Found MR 70.09
$C_7H_{17}O_2PS_3$.	Calculated %:	P 11.92	Calculated MR 70.37

S-Ethylthio-O,O-diethyldithiophosphate was prepared from 26.9 g (0.12 mole) potassium diethyldithiophosphate and 12.5 g (0.12 mole) ethylsulfenyl chloride. B. p. 106-107° (3 mm); n_D^{20} 1.5431; d_4^{20} 1.1810; yield 11.2 g (35% of the theoretical).

*For calculation of the MR for the three sulfur atoms the value of 27.70 derived in this investigation was assumed.

	Found %: P 12.78; 12.74	Found MR 65.76
$C_6H_{15}O_2PS_3$.	Calculated %: P 12.60	Calculated MR 65.78

S-Ethylthio-O,O-diisopropyldithiophosphate was prepared from 11.8 g (0.05 mole) sodium diisopropyldithiophosphate and 7.7 g (0.08 mole) ethylsulfenyl chloride. B.p. 117-118° (3.5 mm); n_D^{20} 1.5240; d_4^{20} 1.1189; yield 6.6 g (48% of the theoretical).

	Found %: P 11.25; 11.12	Found MR 75.05
$C_8H_{19}O_2PS_3$.	Calculated %: P 11.31	Calculated MR 75.00

S-Butylthio-O,O-diethyldithiophosphate was prepared from 11 g (0.05 mole) potassium diethyldithiophosphate and 6.05 g (0.05 mole) butylsulfenyl chloride. B.p. 139.5-140° (3.5 mm); n_D^{20} 1.5306; d_4^{20} 1.1246; yield 3.9 g (30% of the theoretical).

	Found %: P 11.17; 10.82	Found MR 75.33
$C_8H_{19}O_2PS_3$.	Calculated %: P 11.31	Calculated MR 75.00

S-Ethylthio-O,O-diisobutyldithiophosphate was prepared from 26.4 g (0.1 mole) sodium diisobutyldithiophosphate and 12 g (0.12 mole) ethylsulfenyl chloride. B. p. 129-130° (2.5 mm); n_D^{20} 1.5183; d_4^{20} 1.0866; yield 6.6 g (22% of the theoretical).

	Found %: P 10.38; 10.11	Found MR 84.39
$C_{10}H_{23}O_2PS_3$.	Calculated %: P 10.36	Calculated MR 84.24

S-Methylthio-O,O-diisopropyldithiophosphate was prepared from 5.9 g (0.025 mole) of sodium diisopropyldithiophosphate and 2.35 g (0.025 mole) methylsulfenyl chloride. B.p. 99-100° (2 mm); n_D^{20} 1.5297; d_4^{20} 1.1471; yield 3.5 g (60% of theoretical).

Found %: P 11.96; 11.93	Found MR 70.09
Calculated %: P 11.92	Calculated MR 70.37

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* See Consultants Bureau Translation, p. 369.

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SYNTHESIS AND TRANSFORMATIONS OF ORGANOSILICON COMPOUNDS

COMMUNICATION 1. SYNTHESIS OF THE VINYL ETHER OF γ-HYDROXYPROPYLTRIMETHYLSILANE

M. F. Shostakovsky and I. A. Shikhiev

The synthesis and properties of vinyl ethers of organosilicon alcohols and silanols present great interest for synthetic organic chemistry. We are interested in the first place in vinyl ethers of silicoalcohols with the following general structure: $R_3Si(CH_2)_n-OH$, where R may be alkyl, aryl, or alkaryl, and n=1,2,3, etc.

The synthesis of vinyl ethers of silicoalcohols can evidently be carried out in principle by the following routes:

$$HC\equiv CH + R_3Si(CH_2)_n-OH \rightarrow R_3Si(CH_2)_n-O-CH=CH_2$$

$$CH_2=CHCl + NaO(CH_2)_nSiR_3 \rightarrow R_3Si(CH_2)_n-O-CH=CH_2$$

Up to now the vinylation of silicoalcohols has not been described in the literature. The purpose of the present research is to study the possibility of vinylation of silicoalcohols by the method of Favorsky and Shostakovsky [1].

With the objective of studying the properties and transformations of vinyl ethers containing silicon, we resolved to prepare the vinyl ethers of silicoalcohols the character of the hydroxyl group of which is similar to that of the corresponding purely organic alcohols. On this basis we set ourselves the task of studying the vinylation of the alcohol with the following structure: $(CH_3)_3SiCH_2-CH_2-CH_2OH$.

We effected the vinylation of this alcohol by the method of Favorsky and Shostakovsky. The reaction proceeds according to the following equation:

$$HC\equiv CH + (CH_3)_3SiCH_2-CH_2-CH_2OH \rightarrow (CH_3)_3SiCH_2-CH_2-CH_2-O-CH=CH_2.$$

The resultant γ-hydroxypropyltrimethylsilyl vinyl ether was characterized by its physicochemical constants. In addition its structure was confirmed by hydrolysis, which proceeds as follows:

$$(CH_3)_3SiCH_2-CH_2-CH_2-O-CH=CH_2 \xrightarrow{HOH} CH_3-\overset{\overset{O}{\|}}{C}-H + (CH_3)_3SiCH_2-CH_2-CH_2OH.$$

EXPERIMENTAL*

1. Synthesis of γ-hydroxypropyltrimethylsilane $(CH_3)_3SiCH_2-CH_2-CH_2OH$

Into a flask containing Grignard reagent (prepared from 24 g (1 mole) magnesium in 800 ml absolute ether and 122 g (1 mole) α-chloromethyltrimethylsilane [2], cooled to −6°, was slowly passed (with constant stirring) over a period of 2 1/2 hours 84 g (2 moles) dry gaseous ethylene oxide. Since the reaction proceeded with violence, the temperature of the mixture was kept at about +8°. The reaction mass was left overnight. The next day the solid complex was decomposed, first with crude ether and then with 10% hydrochloric acid.

The ethereal layer was separated from the aqueous layer; the latter was extracted with ether and added to the upper ether layer.

The ethereal solution was washed with 1% aqueous sodium carbonate solution and then with water and dried over calcined potassium carbonate. After driving off the ether, the residue (128 g) was vacuum-distilled at 11-12 mm to give:

*Senior Technician Z. S. Volkova participated in the experimental work.

Fraction I	B.p. to 54°;	7.4 g;	n_D^{20} 1.4260
Fraction II	B.p. 55-63°;	21.8 g;	n_D^{20} 1.4296
Fraction III	B.p. 64-65°;	90.5 g;	n_D^{20} 1.4298
	Residue	3 g	

Fractions II and III were combined and redistilled to give 102 g (yield 77.3% of the theoretical) of a fraction with b.p. 62-63 (10 mm). It had the constants*: n_D^{20} 1.4298; d_4^{20} 0.8408; and consisted of γ-hydroxypropyltrimethylsilane.

2. Synthesis of γ-hydroxypropyltrimethylsilyl vinyl ether $(CH_3)_3SiCH_2-CH_2-CH_2-O-CH=CH_2$

20 g γ-hydroxypropyltrimethylsilane [b.p. 62-63° (10 mm), d_4^{20} 0.8408; n_D^{20} 1.4298], 2 g pulverized KOH and 60 g absolute dioxane were charged into a steel rotating autoclave of 0.5 liter capacity. The air was purged from the autoclave by a stream of acetylene and the autoclave was filled with acetylene from a cylinder under a pressure of 18-20 atm. until the reaction mixture was completely saturated with it at the indicated pressure at room temperature and with constant stirring. The reaction mixture was then heated to 180° and the reaction continued for 8 hours. The next day the autoclave was discharged, the product being obtained in the form of a darkish liquid which was washed 5 times with water and dried over sodium sulfate. Three distillations in vacuum gave a fraction with b.p. 60° (18 mm); n_D^{20} 1.4286, d_4^{20} 0.8168.

	Found	MR 49.92
$C_8H_{18}SiO$	Calculated	MR 50.10

	Found %:	C 60.66; 60.77; H 11.38; 11.10; Si 18.39; 18.60
$C_8H_{18}SiO$	Calculated %:	C 60.69; H 11.46 Si 17.72

The above data agree with the formula for γ-hydroxypropyltrimethylsilyl vinyl ether, the mean yield of which from a series of experiments was 35%. γ Hydroxypropyltrimethylsilyl vinyl ether is a transparent mobile liquid with a characteristic ethereal odor. It decolorizes a weak solution of $KMnO_4$ and bromine water. The conditions for its polymerization are being studied.

3. Hydrolysis of γ-hydroxypropyltrimethylsilyl vinyl ether

A weighed amount of the vinyl ether is put into a flask to which is added 25 ml 2% sulfuric acid and 25 ml 0.2 N sodium bisulfite; the flask is shaken until there is complete solution at 24°. At the end of 45 minutes the excess of sodium bisulfite is titrated with 0.1 N iodine.

Found acetaldehyde 90.58; 92.85% of the theoretical.

SUMMARY

1. Using γ-hydroxypropyltrimethylsilane as model substance, the possibility was established of vinylation of silicoalcohols by the method of Favorsky and Shostakovsky. γ-Hydroxypropyltrimethylsilyl vinyl ether was thus obtained.

2. The structure of γ-hydroxypropyltrimethylsilyl vinyl ether was confirmed by its hydrolytic cleavage.

3. Details are given of a method for preparation of γ-hydroxypropyltrimethylsilane and its stability to caustic alkalies is demonstrated.

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CHRONICLE

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On March 25 in the Institute of Physical Chemistry of the Academy of Sciences USSR was held the annual conference of the institute at which Institute Director, Corresponding Member of the Acad. Sci. USSR, V.I. Spitsyn submitted a report on the over-all researches of 1953 and on some perspectives of research in 1954.

V. I. Spitsyn pointed out that in 1953 the greatest developments took place on problems traditionally associated with the institute and whose scope had expanded in the course of a number of years. These relate to investigations of surface phenomena and surface forces, the study of heterogeneous catalysis, the analysis of problems associated with the mechanism and kinetics of electrochemical processes, the study of corrosion processes and methods for combating them, as well as the new directions of research, developed in recent years, associated with problems of chromatography and radiochemistry. The report revealed the achievments of the institute both in respect of individual problems and of the plan as a whole. The reporter wished all concerned success in the achievement of new and theoretically valuable and economically useful results.

Corresponding Member of the Acad. Sci. USSR B.V. Deryagin in his address on the theme of : " The role of surface forces in the kinetics of heterogeneous systems " demonstrated from a unified and general standpoint the value of investigations of surface molecular and electrical forces for the examination and understanding of the mechanism and kinetics of processes in heterogeneous systems with variation of the magnitude or state of the surfaces of separation of the phases and without appreciable change of the masses and composition of the individual substances in the system. The opposite case of processes leading to changes of mass or composition of the components of the system (these include processes of corrosion, evaporation, condensation, topochemical processes, many electrochemical processes, catalytic processes, etc.) were classed by the reporter as first order processes in which the surface forces do not always play a decisive part, while in the case of equilibria they never do so.

With the help of a number of examples of practical value, he analyzed the decisive role of surface forces in the kinetics of first-order processes belonging to the category of surface phenomena proper. B. V. Deryagin drew attention to the specific role of surface forces in coagulation and adhesion of colloidal and dispersed substances, especially in liquid media. Precise information about this role became available after he and his coworkers, in 1934-37, detected and investigated the effect which they called the " wedging" pressure of thin films and which created an energy barrier hindering the approach of molecules to distances at which the resultant of the intermolecular attractions predominates.

The theory developed could be generalized for the case of coagulation of mixtures of colloids and the cohesion of diverse particles after establishment of the characteristics of these problems which are valuable for the theory of dyeing of fibers, the sizing of paper and other practical problems. Applying the same considerations, it was possible to bring precision to the theory of adhesion of bubbles to mineral particles which constitutes the basis of flotation of useful minerals.

Greater precision of the theory of coagulation requires clarification of the course of weakening of molecular forces between interacting surfaces. This problem was treated by carrying out direct measurements of the attractive forces between quartz and glass plates separated by an air space of the order of 10^{-5} cm and higher. These measurements led to important theoretical conclusions, in particular concerning the small influence of molecular forces on the velocity of coagulation of aerosols.

B. V. Deryagin showed that the adhesion of glue and protective films should be treated as a kinetic phenomenon; the thermodynamic approach leads to deviations from experimental results of 100-1000 times and more. The reporter pointed out the great current significance of the study of surface forces both for theory and for a number of very important national economic problems.

Doctor of Chemical Sciences A. V. Kiselev reported on " Adsorption on crystals and colloids" and showed that the current state of the science of adsorption is characterized by : 1) A gap between theoretical investigations of the external surfaces of crystals and the study of adsorption on the internal surfaces of porous bodies. Such a position not only

hinders the investigation of adsorption on the porous adsorbents and catalysts of the greatest practical importance but also limits the possibilities of theoretical study of adsorption. 2) Ignorance of the characteristics of the chemical nature and chemical variability of the surfaces of adsorbents.

The experimentally determined values of the adsorption and heat of adsorption of any given substance depend on the size of surface, the pore structure and the surface state of the adsorbent. The most important problem of adsorption is the separate measurement of : a) the transition from the experimentally measured relative magnitudes (per unit weight of surface) to the absolute magnitudes (per unit surface) b) the influence of shrinkage of pores on the absolute magnitudes of adsorption by investigation of these magnitudes for a series of adsorbents of identical character - ranging from nonporous to finely porous; c) chemical changes of the surface with unchanged pore structure.

In this connection A. V. Kiselev and co-workers made a systematic study of the absolute isotherms and heats of adsorption on quartz and silica gels with pore sizes of 200 to 20 A, on aluminosilica gels and on graphitic substances (soots, active carbons).

The reporter spoke of a number of researches which had established that the transition from quartz to large-pore silica gels does not appreciably change the absolute isotherms and heat of adsorption up to the start of capillary condensation . With further contraction of the pores of silica gels, the adsorptive potential is intensified. This intensification becomes extremely marked with reduction of pore size to 50 A, at first for larger molecules (hydrocarbons), and with further contraction of the pores also for small-sized molecules (nitrogen, methyl alcohol). In the case of adsorption of molecules of very small size which are mainly adsorbed at the expense of hydrogen bonds developed over short distances (water molecules), this effect is inappreciable. For adsorption from solutions, pore contraction in a number of cases causes strengthening of selective adsorption, for example in the separation of hydrocarbons. This is manifested by a shift of the maximum of the isotherms and by an increase in the energy of adsorption. Change in the degree of hydration of the surface of silica gels changes their adsorptive properties, particularly in respect of substances capable of forming hydrogen bonds with the hydroxyls of silica gel. On the surface of carbons, a sharp change of the absolute isotherms of adsorption of water vapor and methyl alcohol is caused by change of the degree of oxidation of the surface. In the case of active carbons the influence of the pore structure is superposed on this influence of the chemical nature of the surface.